

# KEYS TO OXIDATION-REDUCTION

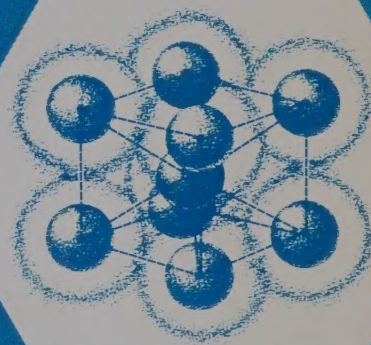
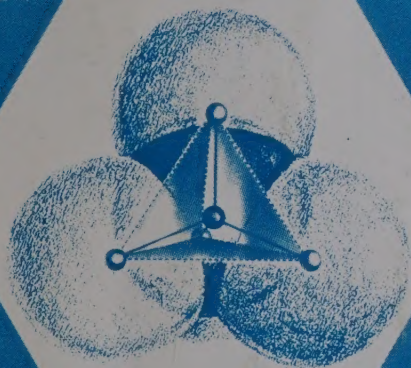
University Of Alberta



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JAY A. YOUNG • ELAINE W. LEDBETTER

A Module in the KEYS TO CHEMISTRY Program



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## RATIONALE FOR MODULES TO KEYS TO CHEMISTRY

The core program of KEYS TO CHEMISTRY is contained in the textbook and laboratory manual. However, it was a part of the basic philosophy of this program that supplementary modules would be developed to do the following things: (1) to expose interested and capable students to more sophisticated concepts in chemistry; (2) to provide remedial work for students who might be deficient in basic skills; and (3) to offer a variety of options for students in the fields of environmental chemistry, practical applications of chemistry in daily living, and interesting by-ways which might lead to hobbies and/or avocations that are chemistry-related. By selecting the modules that fit his or her own goals and interests, the student can plan a truly individualized chemistry course.

Each KEYS TO CHEMISTRY module is like a chapter of the core textbook plus appropriate laboratory exercises. The lab exercises are interspersed with the reading material throughout the module. The modules open with a list of objectives and a

suggested order of study. They conclude with suggestions for creative work and creative writing, a set of practice exercises based on the objectives, a self-test also based on the objectives, a bibliography, and finally, answers to *all* practice exercises and self-test items. Final evaluation can then be made by the student and teacher.

As we view it, KEYS TO OXIDATION-REDUCTION fits into the first of the three categories mentioned. Although oxidation-reduction is not considered in the core program, it is an important aspect of introductory chemistry for those who are more capable and interested. This module is not designed to include voltage calculations,  $E^\circ$ , etc., although a bibliography is included that would lead students inclined in this direction into these more sophisticated topics. The module may be studied anytime after completion of chapter 8 of the core textbook.

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# KEYS TO OXIDATION-REDUCTION

JAY A. YOUNG • ELAINE W. LEDBETTER

A Module in the KEYS TO CHEMISTRY Program

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**OBJECTIVES:**

By the time you have completed your study of this module, you will be expected to demonstrate acceptable performance on the following learning objectives:

1. Write half-equations for the oxidation of any metal you have worked with and for the reduction of its ion(s).
2. Write half-equations for the oxidation and reduction of water.
3. Combine half-equations to write a balanced complete equation for any reaction that you have studied.
- 7-1 4. Apply the rules for assigning oxidation numbers and determine the oxidation number for each element in a formula.
- 7-2 5. Given a complete equation for any oxidation-reduction reaction you have studied, determine what was oxidized and what was reduced in the reaction.
- 7-2 6. Be able to describe how you would determine experimentally which of two metals is more easily oxidized.
- 7-3 7. Discuss at least five areas in which oxidation and reduction are important in daily life and/or in industrial processes.
- 7-3 8. Given a labeled diagram of an electrical cell which includes a salt bridge, identify the following: electrodes, ions being reduced, metal being oxidized, regions in which ions are present, regions of electron flow.
- 7-4 { 9. Explain why a metal loses weight when it is oxidized.
- 7-4 { 10. Explain why a metal gains weight when it is put into a solution of its own ions and the ions are reduced.
- 7-4 11. Apply the principles of oxidation-reduction to explain why iron rusts.
- 3-9 12. Apply the principles of oxidation-reduction to explain how silverware and jewelry are plated.
13. Describe a method for "counting" electrons.

**SUGGESTED ORDER OF STUDY:**

1. Perform Redox Experiment 1 and hand in a formal report.
2. Study Redox Secs. 1 through 4.
3. Perform Redox Experiment 2 and hand in a formal report.
4. Study Redox Sec. 5.
5. Perform Redox Experiment 3 and hand in a formal report.
6. Study Redox Sec. 6.
7. Perform Redox Experiment 4 and hand in a formal report.
8. Study Redox Sec. 7.
9. Perform Redox Experiment 5 and hand in a formal report.
10. Perform Redox Experiment 6 and hand in a formal report.
11. Study Redox Sec. 8.
12. Perform Redox Experiment 7 and hand in a formal report.
13. Study Redox Sec. 9.
14. Perform Redox Experiment 8 and hand in a formal report.
15. Study Redox Sec. 10.
16. Perform Redox Experiment 9 and hand in a formal report.
17. If option is elected, perform Redox Experiments 10 and/or 11 and hand in a formal report.
18. If option is elected, study Redox Sec. 11.
19. If option is elected, perform Redox Experiment 12 and hand in a formal report.

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20. Perform Redox Experiment 13 and hand in a formal report.
21. Perform Redox Experiment 14 and hand in a formal report.
22. Study Redox Sec. 12.
23. Perform Redox Experiment 15 and hand in a formal report.
24. Study Redox Sec. 13.
25. Perform Redox Experiment 16 and hand in a formal report.
26. Study Redox Sec. 14.
27. Perform Redox Experiment 17 and hand in a formal report.
28. Plan creative work, do creative writing, explore outside references.
29. Do the Practice Exercises and review as needed.
30. Take the Self-Test and review further if needed.
31. Check with your teacher for evaluation of your learning experience with this module.

## REDOX EXPERIMENT 1 • LET THERE BE LIGHT!

### Purpose:

To learn how simple cells are made and to construct different cells and observe their operation.

### Materials:

- 2 alligator clips
- 2 15-cm pieces copper wire, not insulated
- 1 15-cm x 5-mm strip of copper foil or a third piece of copper wire
- 15 cm magnesium ribbon
- 3 150-mm x 18-mm test tubes
- 1 watch glass
- 1 small piece of emery cloth
- 1 photographic flash bulb or 1.5-volt flashlight bulb (single-cell type)
- litmus or Hydrion pH test paper
- 25 cc 1M HCL
- 25 cc 1M  $\text{Na}_2\text{SO}_4$  solution
- 25 cc 1M  $\text{CuCl}_2$  solution
- 25 cc water
- 1 sterling silver or silver-plated spoon
- 1 iron nail
- few cc detergent solution
- 1 ringstand
- 1 clamp
- 1 test tube rack
- 2 rubber bands
- 3 wooden tongue depressors



# Procedure:

## PART I

1. Fill one test tube almost full with water, another with hydrochloric acid, and the third with copper(II) chloride solution.
2. Clean the magnesium ribbon by dipping it *quickly* into and out of the HCL and then into and out of the water. Clean both ends in this manner. Record your observations.
3. Clean the copper strip by scouring it with emery cloth. Rinse off any particles of emery cloth that might adhere to the wire by dipping it into and out of the HCL and rinse it with water. Record observations.

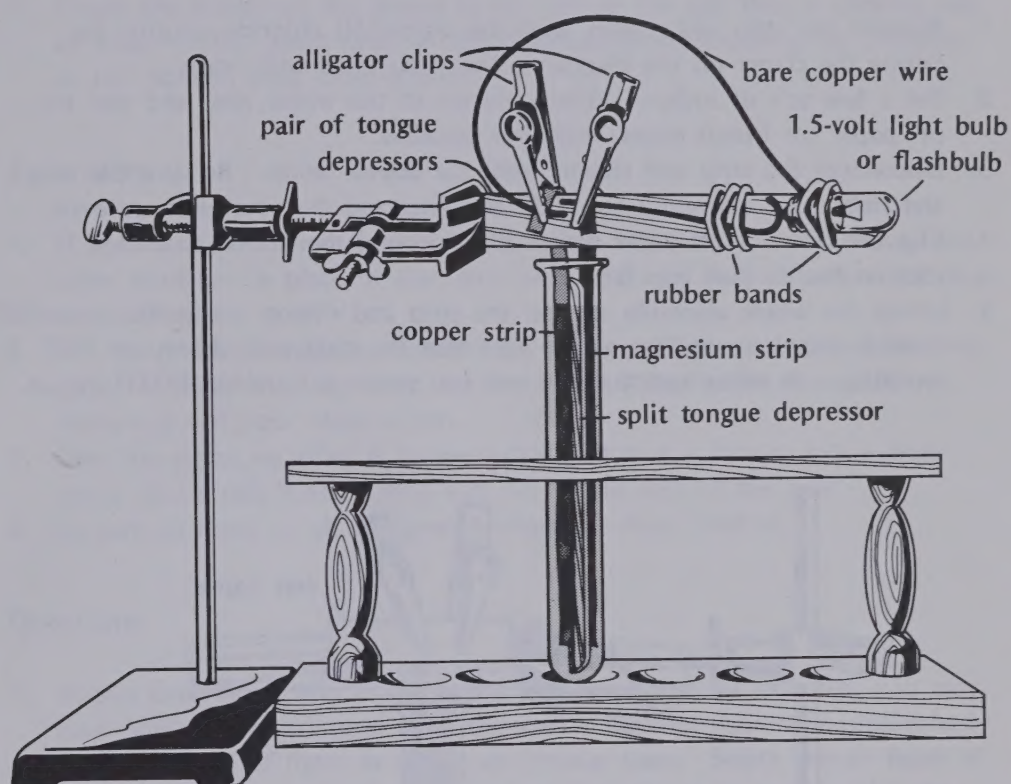


FIGURE A

4. Refer to Fig. A as you carry out the following steps. Place the clamp on the ringstand and clamp together the ends of a pair of tongue depressors.
5. Slip one end of the copper strip between the tongue depressors and attach it to one of the copper wires, using an alligator clip.
6. Examine the bulb. Notice that it has *two* pieces of metal on the outside: one protrudes from the bottom and one goes around the side. These two pieces are the two *terminals* of the bulb.
7. Wrap the free end of the copper wire around the side terminal of the bulb. Fasten the bulb to the free ends of the tongue depressors with a rubber band.
8. Slip one end of the magnesium ribbon between the tongue depressors and attach to the other copper wire, using the second alligator clip.
9. Place the free end of the wire against the bottom terminal of the bulb, using another rubber band to hold the wire in place, as shown in Fig. A.



10. Arrange the copper strip and the magnesium ribbon so they are close together and held firmly by the clips and tongue depressors. They need to be close enough together to be inserted into a test tube, and yet not touch. A tongue depressor split lengthwise and inserted in the test tube as a divider will assure that the strip and ribbon will remain separated.
11. Check that neither the copper wires nor the alligator clips touch each other, and that each wire touches only one clip and only one bulb terminal.
12. Immerse the free ends of the copper strip and the magnesium ribbon in the copper(II) chloride solution, on opposite sides of the split tongue depressor. Record observations.

## PART II

1. Remove the strip and ribbon from the copper(II) chloride solution by raising the clamp on the ringstand, and rinse them with water.
2. Put a few cc's of sodium sulfate solution in the watch glass and wet the pH paper (or litmus paper) with this solution.
3. Disconnect the strip and ribbon from the copper wires. Be sure the strip and ribbon are still close but NOT touching and that the ends are even.
4. Clip the wet pH test paper across the strip and the ribbon so that it touches both. (See Fig. B.)
5. Lower the whole assembly so that the strip and ribbon are in the copper(II) chloride solution once again. Be sure that the strip and ribbon are NOT touching each other and that the wet test paper is touching BOTH metals.

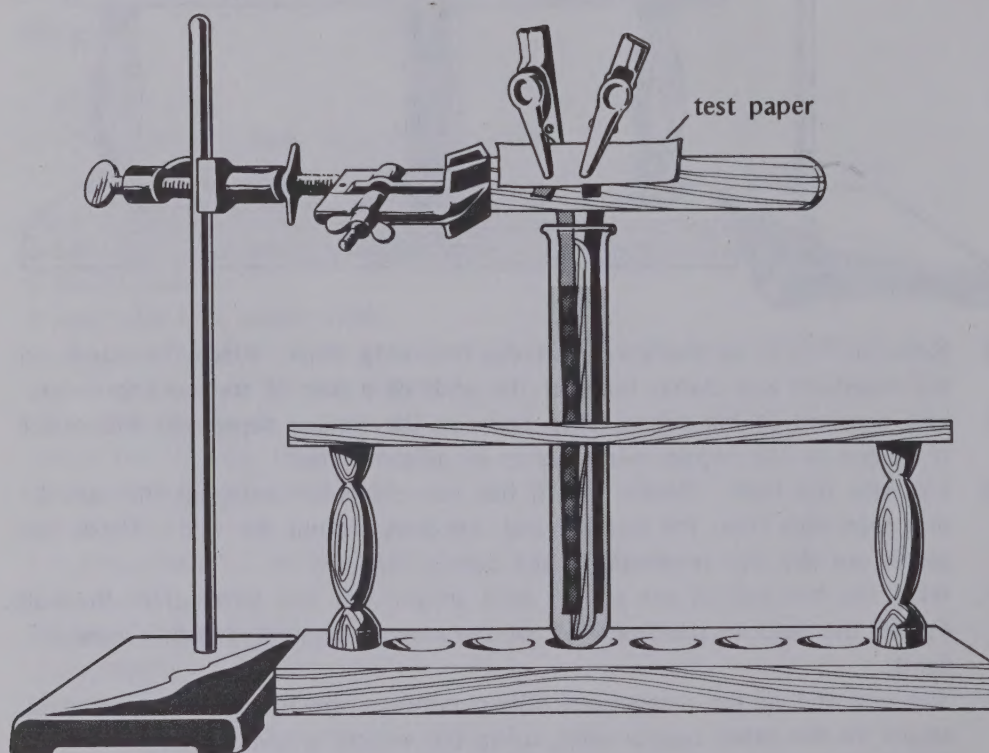


FIGURE B



6. Leave the materials in this manner for about one minute, then withdraw the strip and ribbon from the solution.
7. Remove the test paper and examine it. Record your observations.

### PART III

1. Scour the iron nail with emery cloth. Wash both the nail and spoon with detergent solution and rinse well.
2. Put the bowl of the spoon in your mouth along the side of your tongue. Let the handle stick out.
3. Do the same with the nail, but on the opposite side of your tongue. Let half the nail stick out of your mouth.
4. Touch the handle of the spoon to the end of the nail that is sticking out of your mouth. Hold them in this position firmly touching for a minute or so. Record your observations.

### Extensions

1. If you have permission to do so, you might wish to try other metals and other solutions in place of the ones used. Be sure that all metals are clean and shining.
2. If a voltmeter is available, measure the voltage difference between the two pieces of metal you use when the metals are immersed in the solution. Always record your observations.
3. One interesting variation is to use a fruit, such as a lemon, and a clean penny and a nail inserted into slits cut in the skin of the fruit.
4. Be sure to clean up all equipment when you have finished.

### Questions

1. In this experiment you made several observations. For example, you may have noticed the evolution of a gas, seen a flash of light or a continuously glowing source of light, or noted an unusual taste. Select one or more of these observations and suggest your own hypotheses to explain why they happened.
2. Why did you have to take care that certain things did not touch each other? What do you think might have happened if they did? Test your answer.

## REDOX SECTION 1 • OXIDATION AND REDUCTION

As you now know, the magnesium ribbon, copper strip, and copper(II) chloride solution did something which caused the flash bulb to flash, or the light bulb to glow. To understand what happened inside the copper(II) chloride solution, we must first know what an electric current is.

An *electric current* is a flow, or movement, of electrons through a conductor. As Fig. C shows, electrons in the magnesium ribbon moved up and out, through



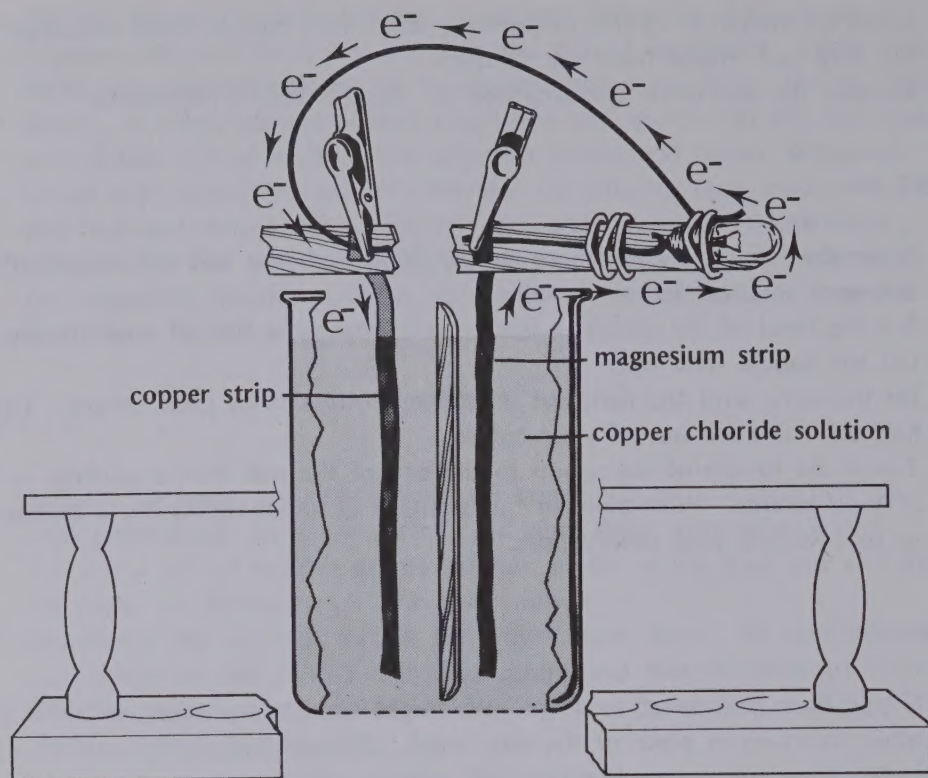


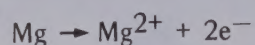
FIGURE C

the attached alligator clip, into the short wire attached to the bulb, through the bulb, out the other wire, through the second alligator clip, and into the copper strip, where something happened to them. As these electrons moved through the bulb, it flashed or glowed (depending upon which kind of bulb it was).

The test tube of copper(II) chloride solution with the magnesium ribbon and copper strip in it is an example of a *cell*. The two metal strips—the magnesium ribbon and the copper strip—are *electrodes*. When the electrodes were connected to the bulb, a closed *electric circuit* was formed. There was an electric current in the circuit as electrons moved from the magnesium electrode through the bulb and into the copper electrode.

### Loss of Electrons

The electrons left the cell from the magnesium electrode. The equation describing the reaction at this electrode is



Magnesium atoms each gave up two electrons and became magnesium ions,  $\text{Mg}^{2+}$ .

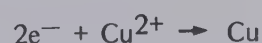
What happened to the magnesium ions? Perhaps you noticed that the magnesium ribbon looked a bit ragged after it was used. If you had weighed it before and after, you would probably have found that it weighed considerably less after the experiment. A chemical test for magnesium ions like the one you performed back in Exp. 5-2 would show the presence of magnesium ions in solution at the end of Redox Experiment 1. So we conclude that as the magnesium atoms became magnesium ions, they entered the copper(II) chloride solution.



Meanwhile, what happened to the electrons? As electrons began to collect on the ribbon, they pushed each other away because of their similar electric charges, and some moved into the alligator clip and beyond into the rest of the circuit. As they moved, they pushed the electrons on the clip and the wires ahead of them, in a sort of chain reaction—just as someone in a crowd of people trying to leave a theater might push on the people ahead and set off a chain reaction of pushes. Finally (really, after a split second) electrons began to move onto the copper electrode.

### Gain of Electrons

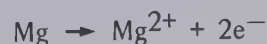
At the copper electrode electrons entered the cell. What happened to the electrons as they started to collect on the copper electrode? Copper(II) ions from the copper(II) chloride solution gained electrons, two each, and became copper atoms. The equation describing the reaction at the copper electrode is



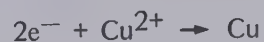
If you had weighed the copper strip before and after you performed Redox Experiment 1, you would probably have discovered that it gained weight during the experiment. As the copper(II) ions combined with the electrons, they came out of solution and were deposited as copper atoms on the copper electrode. As you might guess, a chemical test for the concentration of copper(II) ions in the copper(II) chloride solution would show a reduction in the amount of copper(II) ions during the experiment. For this reason the copper(II) ions are said to be *reduced*, although the term *reduced* has come to have a more general meaning, as you will learn shortly.

### Half-Reactions

There were two reactions going on at once in Redox Experiment 1. One involved a loss of electrons:



The other involved a gain of electrons:



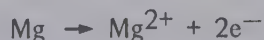
The first reaction, in which a neutral atom lost electrons, is called an *oxidation half-reaction*. The second, in which a positive ion gained electrons and became a neutral atom, is called a *reduction half-reaction*. It may seem contradictory for the reduction half-reaction to be the one in which the copper *gains* electrons and the weight of the copper strip *increases*. Just remember that the name comes from the reduction in the concentration of copper ions in the solution; the copper ions leave the solution by gaining electrons and depositing on the copper strip.



Notice that an oxidation and a reduction took place at the same time. In the oxidation process, electrons were lost by magnesium atoms. These electrons were gained by the copper ions in the reduction process. The entire process is called an *oxidation-reduction reaction*, or *redox reaction* for short.

In Redox Experiment 1 you may also have noticed bubbles of gas that formed on the magnesium ribbon. This is evidence for another pair of oxidation and reduction half-reactions that have nothing to do with the flow of electrons through the bulb. This second case involves magnesium atoms and water molecules.

The oxidation half-reaction can be described by the same equation as the first oxidation half-reaction:



The water molecules near the magnesium ribbon pick up the electrons, producing hydrogen gas and hydroxide ions:

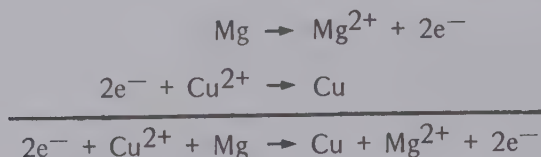


This is the reduction half-reaction. Equations like these are called *half-equations* because they describe half-reactions.

Again, notice that an oxidation and a reduction took place at the same time. Magnesium was oxidized and water was reduced. Neither half-reaction can take place by itself.

### Addition of Half-Equations

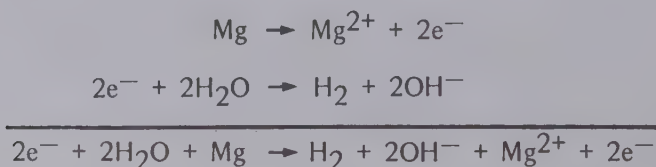
We can add the half-equations for two half-reactions that occur together to get a complete equation that describes the total event. For the first case:



Since the symbol for two moles of electrons,  $2\text{e}^{-}$ , appears on both the left and right of the arrow, it can be dropped to give us an ordinary appearing chemical equation:

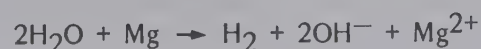


For the second case:





Again we can drop the  $2e^-$  symbol on both sides of the arrow:



## REDOX SECTION 2 • HOW TO TELL WHAT IS OXIDIZED AND WHAT IS REDUCED

Suppose that you knew that magnesium reacts with water to produce gaseous hydrogen, magnesium ions, and hydroxide ions, but you did not know the two half-equations for this total reaction. How could you tell whether oxidation and reduction is taking place, and if so, what is oxidized and what is reduced? To answer this, we need better definitions of oxidation and reduction. In these new definitions, *oxidation is defined as an increase in oxidation number; reduction is defined as a decrease in oxidation number.*

### Rules and Examples

To apply these new definitions, we need some rules. (You will recognize that a few of these are the same rules you learned in your study of Chapter 8 of the *Keys to Chemistry* text.)

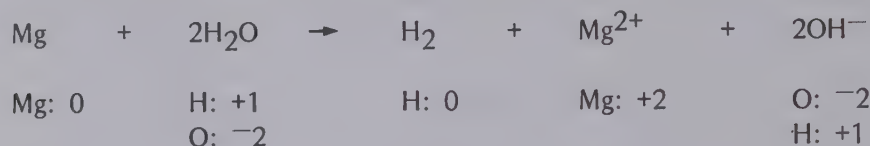
1. The oxidation number of a one-element ion is the same as the charge on the ion, except that the plus or minus sign is written *in front of* the oxidation number.  
*Example:*  $Mg^{2+}$ . This ion is composed of one element with a charge of  $2+$ . So, the oxidation number of magnesium ion is  $+2$ .
2. The oxidation number of an uncombined element, or one combined with itself only, is zero.  
*Example:* Mg. An uncombined element, its oxidation number is zero.  
 $H_2$ . One hydrogen combined with another hydrogen -- with another similar atom, with itself; its oxidation number is zero.
3. The oxidation number of a multiple-element ion is the same as the charge on the ion (except for switching the position of the plus or minus sign); the oxidation numbers of each element in the ion must add up to the oxidation number of the ion.  
*Example:*  $OH^-$ . The charge is  $1^-$ , so the oxidation number of the whole ion is  $-1$ . The oxidation numbers of the oxygen and hydrogen, in the ion, might be different from  $-1$ ; whatever they are, they have to add up to  $-1$ . To find out what they are, check Table 8-1 in the text. In that table, the common oxidation numbers are  $-2$  for oxygen and  $+1$  for hydrogen. This checks out nicely, since  $-2$  and  $+1$  add up to  $-1$ .
4. The oxidation number of a neutral molecule is zero, but the oxidation numbers of the elements in the compound, whatever they are, must add up to zero.  
*Example:*  $H_2O$ . Check Table 8-1 in the text. The common oxidation numbers are  $-2$  for oxygen and  $+1$  for hydrogen. So,



we add  $-2$ ,  $+1$ , and  $+1$  (two  $+1$ 's, one for each hydrogen) and get zero, which checks nicely.

### Using the Rules

Now we can use the new rules to find out what is oxidized and what is reduced in the equation showing the reaction between magnesium and water. The rules have been used to show the oxidation number of each element in each term of the equation. The elements and oxidation numbers are listed below each term.



Notice that the magnesium changed oxidation number from 0 to  $+2$ . This is an increase; so we know that magnesium was oxidized. Some of the hydrogen changed oxidation number from  $+1$  to 0. This is a decrease; that portion of the hydrogen was reduced. It is more correct to say that some of the hydrogen in the water is reduced (and some is not), rather than saying that the water is reduced. However, either way--"water is reduced" or "some of the hydrogen in the water is reduced"--is acceptable.

Notice also that the oxidation number of the oxygen,  $-2$ , stays the same on both sides of the arrow. The oxygen is neither reduced nor oxidized. Similarly, as we have noticed, the oxidation number of some of the hydrogen,  $+1$ , stays the same, so that a portion of the hydrogen is neither reduced nor oxidized.

For practice, try the equation



which was obtained in the last section by adding two half-equations. How can you tell what is oxidized and what is reduced in this equation? Apply the rules and use Table 8-1 from the text if necessary. Copy the equation in your notebook, and write the correct oxidation numbers below each term. You will then notice that magnesium increases its oxidation number from 0 to  $+2$ ; it is oxidized. Copper ion is reduced, from an oxidation number of  $+2$  to 0.

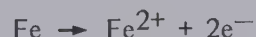
### REDOX SECTION 3 • A REVIEW

Let us review what we have learned thus far. Some reactions, not all, are reactions in which both an oxidation and a reduction occur. We can define oxidation and reduction in two ways: 1) oxidation is a loss of electrons and reduction is a gain of electrons; or, 2) oxidation is an increase of oxidation number and reduction is a decrease of oxidation number.

When we write the two half-equations for a reaction, the loss or gain of electrons is clearly shown in each half-equation. When we write the complete equation, the electron symbols cancel, so their loss or gain is not clearly shown. When we start with a complete equation, we must figure out what is oxidized and what is reduced by using the rules and the information in Table 8-1 from the text.



For example, the following half-reactions took place in your mouth when you inserted the iron nail and the silver (or silver-coated) spoon. Iron was oxidized:



In the vicinity of the spoon, water in your saliva was reduced:

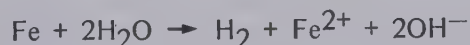


The hydrogen gas is not produced rapidly enough for most people to be able to observe the production of bubbles in their mouth. But an unusual taste is observable. This sensation is probably due to a combination of things: the  $\text{OH}^{-}$  ions, the  $\text{Fe}^{2+}$  ions, and some hydronium ions from the following consequent reaction:



(As you can see, there are no changes in oxidation numbers here, so this consequent reaction is not an oxidation-reduction reaction.)

To continue with the example, notice that the complete oxidation-reduction equation, from the addition of the two half-equations, is



The electrons released by the oxidation of the iron nail passed from the nail to the spoon when they were touched together outside the mouth, then travelled to the bowl of the spoon and reduced the water in the saliva. As you can see, the complete equation describes the oxidation of iron and the reduction of water, but omits specific indication of the loss and gain of electrons. The oxidation of the iron is identified by noticing that its oxidation number changed from zero to +2; the reduction of the water (or of the hydrogen in the water) is identified by noticing that the oxidation number of the hydrogen changed from +1 to zero.

## REDOX SECTION 4 • USING ELECTRON FLOW

In some oxidation-reduction reactions it is possible to force the electrons to flow outside of the place where the electrons are actually lost, or gained. When we do this, we can use the electrical current, the flow of electrons, usefully to light a glowing filament, or flash a flash bulb, or run a motor. In other cases, as with the magnesium and the water, the electrons did not flow away from and back into the place where they were lost and gained, so that we were not able to use them.

The results of experiments such as those you performed, and other experiments; such as the weighing of the electrodes before and after to see which one gained or lost atoms, plus reasonable guesses about which element gained or lost electrons--all this provides a basis for a theoretical description of oxidation-reduction reactions. Still other experiments are needed to form the basis for a more complete theory.

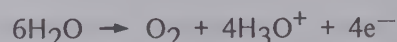


## A Confirming Observation

You performed one of these other experiments with the pH test paper. The paper turned dark green (or blue) where it touched the magnesium ribbon, and reddish (this was harder to see) where it touched the copper strip. According to the theory we have studied here, electrons released in the oxidation of the magnesium atoms moved from the magnesium ribbon into the wet pH test paper where they reacted with the water in the test paper. The water was reduced. (Or, if you prefer, some of the hydrogen in the water was reduced.)



In the presence of the  $OH^{-}$  ions, the test paper turned dark green, or blue (depending upon which brand you used). At the other end of the piece of test paper, where it touched the copper strip and turned reddish, water was oxidized as electrons were lost and entered the copper strip. When water is oxidized, this half-equation applies:



The hydronium ions present in the test paper caused it to become reddish colored.

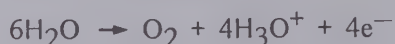
The fact that the test paper turned dark green or blue at the region touching the magnesium ribbon helps to show that the magnesium electrode lost electrons by oxidation, and these electrons reduced the water in that end of the test paper. The fact that the test paper turned reddish at the place where it touched the copper strip helps to show that the water in that end of the test paper lost electrons by oxidation; these electrons then traveled through the copper strip and reduced copper ions to copper atoms in the solution below.

## Two Oxidation-Reduction Reactions

When you used the test paper, then, there were two oxidation-reduction reactions taking place. In the first, magnesium atoms and copper ions were oxidized and reduced, respectively. In the second, water at one end of the test paper was reduced and water at the other end was oxidized. (Sodium sulfate in the solution in the test paper helped to make the oxidation and reduction of the water occur faster than otherwise. If it were not present, or if no ions were present in the water in the test paper, you would still be holding it on the magnesium ribbon and copper strip, waiting for the color change.) We already know the complete equation for one of these oxidation-reduction reactions:



What about the other one? To get it, we should add the two half-equations, one for the oxidation and one for the reduction of water:

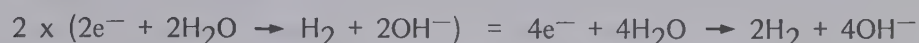




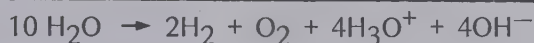
But as you can see, if we add these, the electrons will not cancel out because  $2e^-$  is on one side and  $4e^-$  is on the other. If we add them anyway, the whole equation would say that there are some electrons left over at the end of the reaction. This is not possible. The principle of oxidation and reduction states that we cannot have one without the other, and we cannot have any extra, or deficient, electrons. The number of moles of electrons lost must be equal to the number gained. They must cancel out in the whole equation.

### Multiplying Half-Equations

Fortunately, we can easily solve the problem by indicating that we have twice as many moles in the reduction half-equation as we showed above, so that there will be 4 moles of electrons in each half-equation. Merely multiply the reduction half-equation by two, like this:



Now, we can use this new reduction half-equation, and the electrons will cancel out mathematically.

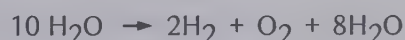


Eventually, the  $OH^-$  ions (which are produced where the electrons from the magnesium electrode interact with water molecules) will be diffused throughout the water solution in the test paper strip. Similarly, the hydronium ions (formed at the place where the paper touches the copper strip) will diffuse. When these two different ions,  $OH^-$  and  $H_3O^+$ , meet, two molecules of water are formed.



### The Complete Equation

In the complete equation for the oxidation and reduction of the water molecules, there are 4 moles of hydronium ions and 4 moles of hydroxide ions. When all the action is finished, these will have combined to produce 8 moles of water molecules. Thus the complete equation can be written:



or, cancelling out eight waters:



This last equation shows all of the hydrogen reduced from +1 to 0, and all of the oxygen oxidized from  $-2$  to 0. Since this is not really what happened,

some chemists prefer to keep things straight by writing the longer equation, which shows that only some of the hydrogen is reduced and some of the oxygen is oxidized.

### A Review

It is time for another review. In some reactions there is no change in oxidation number of the elements involved. In other reactions the oxidation numbers do change. Always, if there is a change in oxidation number there will be two changes, an oxidation, or increase, and a reduction, or decrease. If we wish to show only the oxidation, or only the reduction, we write half-equations, which also show the loss or gain of electrons, respectively. Half-equations can be added to make complete equations; but sometimes it is necessary to multiply one or the other half-equation by a whole number first, so that when the two are added the electrons will cancel mathematically.

## REDOX EXPERIMENT 2 • COMPARING THE TENDENCIES OF TWO METALS TO GIVE UP ELECTRONS

### Purpose:

To compare two metals by studying the relative tendencies of atoms of each metal to give up electrons and of ions of each to gain electrons.

### Materials:

2 test tubes, 150 mm x 18 mm  
1 thermometer  
15 cm magnesium ribbon  
15 cm bare copper wire, or copper strip  
25 cc 1M  $\text{CuCl}_2$  solution  
25 cc 1M  $\text{Mg}(\text{NO}_3)_2$  (or  $\text{MgCl}_2$ ) solution  
emery cloth

### Procedure:

1. Scour both the magnesium ribbon and the copper wire or strip with the emery cloth.
2. Fill one test tube about half full with the copper(II) chloride solution.
3. Immerse the thermometer and note the temperature of the solution.
4. Keep the thermometer in the solution and immerse one end of the magnesium ribbon in the solution. Keep it there for a little less than one minute. Make careful observations and record them.
5. Withdraw the magnesium ribbon and examine it closely. Record observations.
6. Repeat the above procedure after rinsing the thermometer. This time fill the second test tube half full with magnesium nitrate (or magnesium chloride)



solution. Immerse the copper wire in this solution alongside the thermometer. Make careful observations for a minute or so.

7. Withdraw the copper wire and examine it closely. Record observations.
8. Clean apparatus and return it to its proper place.

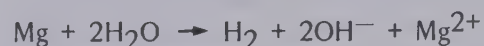
### Questions:

1. In one of the test tubes hydrogen gas was evolved. This was due to a reaction between a metal and water. Identify the test tube and write an equation for the reaction.
2. In one of the test tubes, a deposit appeared on the metal. Identify the test tube, describe the deposit, and write an equation for the reaction.
3. In the equations you wrote for Questions 1 and 2, identify what was oxidized and what was reduced.
4. a. Were Mg atoms oxidized by reducing  $\text{Cu}^{2+}$  ions?  
b. Were Cu atoms oxidized by reducing  $\text{Mg}^{2+}$  ions?
5. Which metal, magnesium or copper, seems to become oxidized more easily? Explain why you selected the metal you did.
6. Which ions, magnesium or copper, seem to become reduced to neutral atoms more easily? Explain why you selected the ions you did.

## REDOX SECTION 5 • DISCUSSION OF REDOX EXPERIMENT 2

In the last experiment you observed that the magnesium ribbon reacted and that a gas was evolved. The gas was hydrogen (you could confirm this by testing for hydrogen). When you removed the magnesium ribbon from the solution, you noticed a reddish brown scum, or deposit, on it. This was a deposit of copper atoms. Perhaps you also observed that the magnesium ribbon edges were irregular, as though some of the magnesium metal had been eaten away.

From this we can conclude that magnesium atoms were oxidized to form electrons and magnesium ions, now in the solution. Some of the electrons reacted with water molecules in the solution to produce hydrogen gas and hydroxide ions. The complete equation for this reaction is one you have seen earlier in Redox Section 2:



Other electrons reacted with copper(II) ions in the solution to reduce them to copper atoms, which appeared as a reddish brown deposit on the magnesium. The complete equation for this reaction is also familiar:



You probably noted an increase in the temperature of the solution. This indicates that heat energy was released during one or both reactions. What about the randomness of the system before and after the reaction? In the reaction involving water molecules, the randomness of the system has increased--for every two moles of water molecules that reacted, one mole of hydrogen molecules was created (and escaped into the atmosphere) *and* two moles of

hydroxide ions were created and remained in the solution. In the other reaction the randomness remained about the same--atoms were replaced by ions and vice versa.

On the other hand, nothing observable happened when the copper wire was immersed in the magnesium nitrate (or magnesium chloride) solution. Apparently, a system of Mg atoms and  $\text{Cu}^{2+}$  ions has a higher potential energy than a system of an equivalent number of  $\text{Mg}^{2+}$  ions and Cu atoms. The only reaction that will occur spontaneously is the one in which the energy of the system decreases (since there is no change in the randomness).

We can try other metals and ions in solution, in Redox Experiment 3.

### REDOX EXPERIMENT 3 • COMPARING THE TENDENCIES OF SEVERAL METALS TO GIVE UP ELECTRONS

It is more complicated experimentally to compare the tendencies of four metals to give up electrons and of four ions to gain electrons. However, you will notice that the basis of the procedure is the same as in the preceding experiment. Because the work is more complicated, keep a very careful record of your observations.

#### Purpose:

To study the relative tendencies among four metals of their atoms to give up electrons and of their ions to gain electrons.

#### Materials:

- 16 150-mm x 18-mm test tubes
- 4 250-cc beakers
- 4 iron nails
- 4 pieces of zinc strip, about the size of the nails
- 4 pieces of lead strip, about the size of the nails
- 4 pieces of bare copper wire, about the size of the nails
- 50 cc of each of the following solutions:

1M  $\text{Zn}(\text{NO}_3)_2$

1M  $\text{FeCl}_3$

1M  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$

1M  $\text{CuSO}_4$

Note: If the lead acetate solution is cloudy, it may be because of the presence of suspended lead hydroxide. If this is true, your teacher can clear it up by adding a very few drops of concentrated nitric acid while stirring.

25 cc 1M HCl

piece of emery cloth

thermometer (optional)



## Procedure:

1. Clean the zinc strips by dipping them into and out of a 1-molar solution of HCl, and rinse them thoroughly with water.
2. Clean the nails and copper wire with emery cloth, rinsing them with HCl and water.
3. Clean the lead strips with emery cloth until they are shining and rinse with water.
4. Put four test tubes in each of the beakers. Label one beaker  $\text{Zn}(\text{NO}_3)_2$ . Half fill each of these four test tubes with the zinc nitrate solution. Place a strip of zinc in one of the half-filled test tubes, a nail in the second, a lead strip in the third, and a piece of copper wire in the fourth.
5. Label the second beaker  $\text{FeCl}_3$ . Half fill each of these test tubes with the iron(III) chloride solution. Place one of each of the different metals in the test tubes.
6. Repeat this procedure for the other two beakers and their test tubes, using lead acetate solution for one beaker and copper sulfate solution for the other.
7. Observe all 16 systems carefully and record your observations. Your data table might be patterned after the sample one in Fig. D, except you will substitute the names of the materials you are now using.

FIGURE D

Ray D'Sum	
Redox Expt - 3	
April 1, 19-	
Solution in test tube, Beaker # 1:	
Musicum Nitrate	
Metal Pieces	Results
Pianoum	Deposited Musicum
Flutissium	Gas evolved
Bassoono	Turned Purple
Frenchhornium	Made noise
Solution in Test tube, Beaker # 2	

8. If you wish to use a thermometer to measure any temperature changes, these should also be recorded. Be sure to rinse the thermometer before inserting it into a different test tube.
9. Look for color changes in the solutions. This may require anywhere from a few minutes to several hours. For example, in water solution copper ions are blue. If a blue solution containing copper ions changes to some other color, we would suspect that the copper ions are no longer present in that

solution. Iron ions sometimes impart a yellow color to a solution. Zinc and lead ions are colorless in water solution.

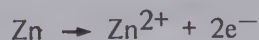
- Clean up all equipment when you have finished your experiment.

### Analysis of Data:

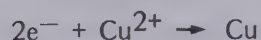
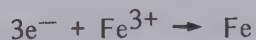
- From your observations deduce the oxidation and reduction half-reactions which probably took place and write the corresponding half-equations. From these, write the complete equations to describe what happened.
- Which metal gives up electrons the most readily of the four? Which the least readily?
- Arrange the four metals in order of ease of being oxidized, listing the *most easily oxidized* metal first.
- Arrange the four metals in order of difficulty of reducing their ions to neutral atoms, listing the *most difficult ion to reduce* first.
- Tell why you would, or would not, expect the list of names in your answer to questions 3 and 4 to be the same.

## REDOX SECTION 6 • LISTING METALS IN ORDER OF EASE OF OXIDIZING

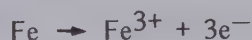
You probably noted that zinc reacted with iron ions, with lead ions, and with copper ions. This oxidation half-equation



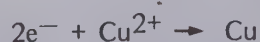
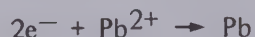
can be paired with each of these reduction half-equations:



Perhaps you noted that iron reacted with lead ions and with copper ions (but not with zinc ions, or iron ions). This oxidation half-equation

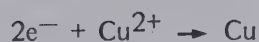
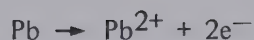


can be paired with each of these reduction half-equations:



Did you observe that lead reacted only with copper ions? These two half-equations can be paired:





And did you find that copper reacted with none of the ions?

### Zinc

Of the four--zinc, iron, lead, and copper--zinc atoms are the most easily oxidized. By getting oxidized, the zinc atoms were able to reduce iron ions, lead ions, and copper ions to neutral atoms.

Zinc ions, on the other hand, are the most difficult to reduce. Neither iron, lead, nor copper atoms reacted with zinc ions to reduce them to neutral atoms.

### Iron

Of the remaining three--iron, lead, and copper--your results show that iron atoms are the most easily oxidized. Iron ions, on the other hand, cannot be reduced by lead or copper atoms; they can be reduced by zinc atoms only (of the four metals).

We could make a vertical column for the four metals, with the easiest to oxidize (zinc) at the top, and the next easiest (iron) under it, like this:

Zinc  
Iron

What would go under the iron in this column, lead or copper? Check your recorded observations and deduce your choice.

### Lead and Copper

If your work was carefully performed, with good observations, you will decide to put lead under iron, and copper last, under lead, like this:

Zinc  
Iron  
Lead  
Copper

Where would magnesium go in such a list? The results of Redox Experiment 2 suggest that magnesium would be somewhere above copper. Perhaps you would like to design your own creative experiment to answer this question. Ask your teacher for permission, but first prepare a set of directions and a list of equipment you will need.

## REDOX EXPERIMENT 4 • HALF-CELLS AND SALT BRIDGES

In this experiment you will make and compare four half-cells. A *half-cell* is a container filled with the solution of a metallic salt (for example, zinc nitrate),

in which there is one electrode of the same metal (zinc, in this example). No visible reaction occurs in a half-cell until it is connected with a half-cell for a different metal. Then an oxidation half-reaction takes place in one half-cell, and a reduction half-reaction in the other. Connecting the half-cells creates an electrical pressure, or *voltage*, that causes electrons to move out of the oxidation half-cell into the reduction half-cell. You will be measuring the voltage with an instrument called a *voltmeter*.

### Purpose:

To identify and compare the oxidation-reduction reactions that occur in different pairs of half-cells by measuring the voltage (electrical pressure) created by each reaction.

### Materials:

- 4 150-mm x 18-mm test tubes
- 50 cc of each of the following solutions:
  - 1M  $\text{Zn}(\text{NO}_3)_2$
  - 1M  $\text{FeCl}_3$
  - 1M  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$
  - 1M  $\text{CuSO}_4$
- 25 cc 1M  $\text{Na}_2\text{SO}_4$  solution
- several 5-mm x 15-cm strips of filter paper
- 1 watch glass
- 1 iron nail
- 1 strip each of zinc and lead (as in Redox Experiment 3)
- 1 piece of bare copper wire or strip
- 1 voltmeter, range 0 to 3 volts or 0 to 10 volts
- 2 lengths of wire (may be insulated)
- 2 alligator clips
- 1 ringstand
- 1 clamp
- 1 tongue depressor
- 1 test tube rack

### Procedure:

1. Clean the metals as you did in Redox Experiment 3.
2. Bend each metal strip into a "J" shape so that the tail of the "J" can be hooked over the top of a test tube.
3. Nearly fill each of the test tubes with one of the following solutions, and label each test tube:
  - test tube 1: zinc nitrate
  - test tube 2: iron(III) chloride
  - test tube 3: lead(II) acetate
  - test tube 4: copper(II) sulfate
4. Place each "J" shaped metal in the solution of its own salt (e.g., zinc in the



zinc nitrate) so that most of each metal is submerged in the solution and the top end is hooked over the top of the test tube. You have now made four half-cells.

5. Attach two wires, one each, to the plus and minus terminals of the voltmeter. Be sure that the wires are shining bright both where they make contact with the terminals and at their free ends.
6. Take any two half-cells and place them close to each other in the test tube rack.
7. Place some sodium sulfate solution in a watch glass and wet a strip of filter paper in it. This will serve as a *salt bridge*, which is something that connects two salt solutions. Drape this paper salt bridge over the mouths of both test-tube half-cells. Be sure that the ends of the salt bridge are in each of the solutions in the half-cells. The set-up is illustrated in Fig. E.

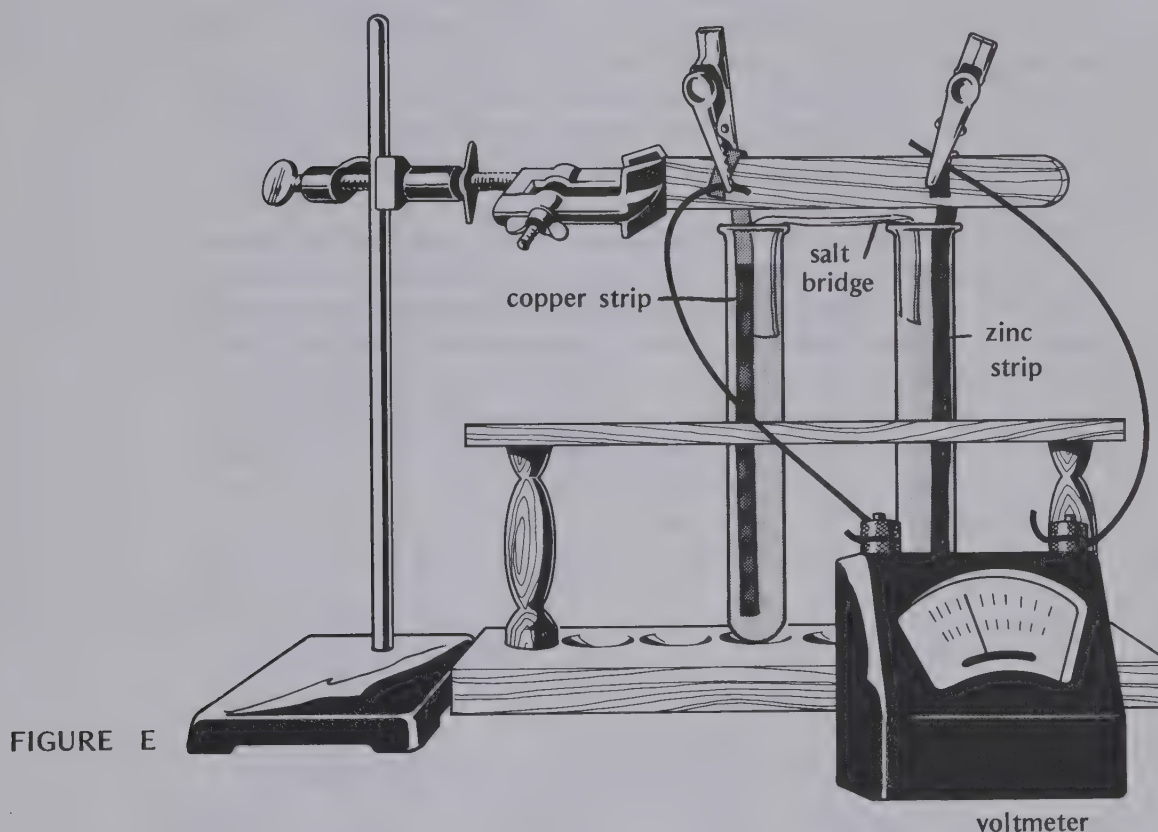


FIGURE E

8. Arrange the ringstand, clamp, and tongue depressor as shown in Fig. E. Lift each metal electrode and hook it over the tongue depressor; with the alligator clip place each metal in contact with the bare, free end of one of the wires attached to the voltmeter terminals.
9. Observe the voltmeter. If the needle tends to go off scale (to the left of the zero), reverse the wires connected to the electrodes, so that each electrode is now connected to the opposite voltmeter terminal. The voltmeter will probably read somewhere around one half volt.
10. Record the voltmeter reading and note which half-cell is connected to the negative voltmeter terminal. If you see any other signs that a reaction is taking place, record them in your notebook.

11. While the voltmeter is giving a reading, remove the salt bridge from the pair of connected half-cells. Observe the voltmeter needle. Put the salt bridge back and again observe the needle.
12. Repeat the measurements for all possible pairs of half-cells, using a fresh salt bridge for each pair. (There are six different combinations of half-cells.)

### Analysis of Data:

1. The voltmeter gives a reading for the voltage when its negative terminal is connected to the half-cell in which electrons (which are negatively charged) are being given off. The giving off of electrons indicates that oxidation is taking place. For each pair of half-cells, indicate the half-cell in which oxidation took place and the half-cell in which reduction took place.
2. For each metal, list the other metals (if any) which caused it to be oxidized when their two half-cells were connected.
3. Make a list of the four metals such that each metal is oxidized by the half-cells of *all* the metals below it in the list, when their two half-cells are connected. The list will then indicate the relative ease of oxidizing of each metal.
4. In the table below, the letters *A*, *B*, *C*, and *D* have been used to indicate the four metals in order of their appearance on the list you made for Question 3. Copy the table, substituting the correct metal for each letter name. Then fill the boxes in with the voltmeter readings for each combination of half-cells.

Oxidation Half-Cell	Reduction Half-Cell		
	Metal B	Metal C	Metal D
Metal A			
Metal B			
Metal C			

5. Study the table you made for Question 4. Does there seem to be a relation between the voltmeter readings and the relative positions of the pair of metals on the list? If so, describe.

### Questions:

1. Consider a half-cell in which there is an oxidation half-reaction. What do you think happens to the electrons lost by the metal through oxidation? And what happens to the positive metallic ions that are formed? Does the solution tend to accumulate an excess positive charge or an excess negative charge?
2. Now consider a half-cell in which there is a reduction half-reaction. What exactly is being reduced in the half-cell? Where do the electrons that are

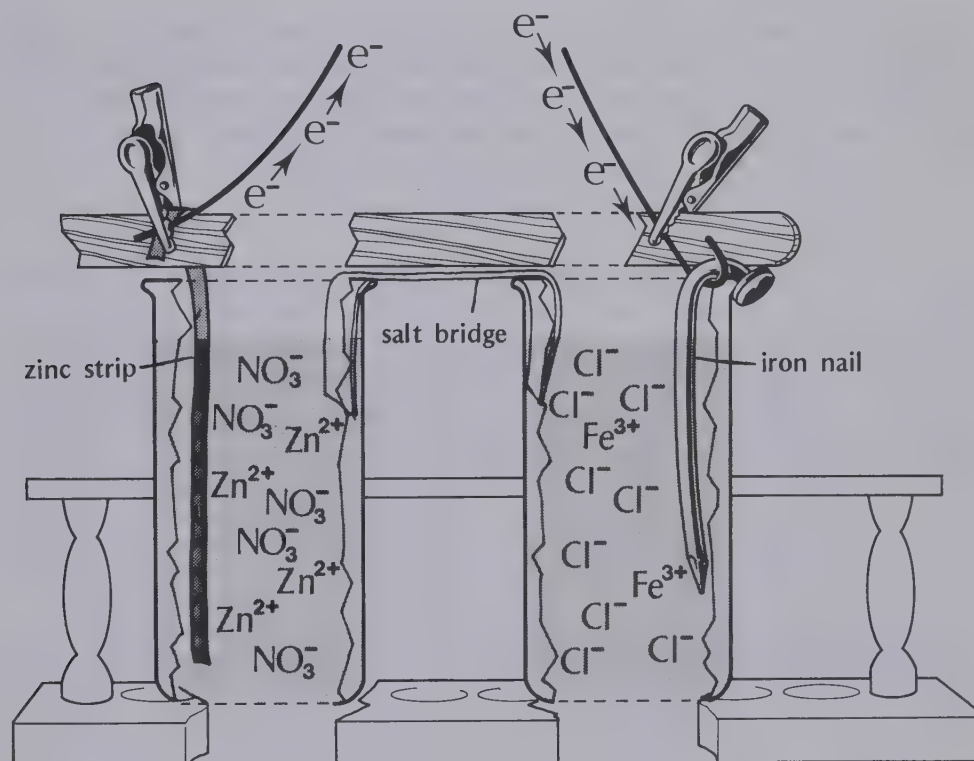


- gained in the half-reaction come from? Does the solution tend to accumulate an excess positive charge or an excess negative charge? Explain.
- What happened to the voltmeter needle when you removed the salt bridge? What happened when you replaced the salt bridge? Why do you think the salt bridge is necessary? Propose a hypothesis that suggests what might possibly move through the salt bridge. How might you test this hypothesis?
  - Compare the list of metals you made in this experiment with the list you made in the last experiment. Are there any similarities? Any differences? Is this what you would expect?

## REDOX SECTION 7 • USEFUL APPLICATIONS: CELLS AND BATTERIES

As you may have guessed, the many different kinds of cells and batteries used in our daily life are based upon the principles you have learned thus far. Before we look at some of these practical cells and batteries, let us review the operation of the pairs of half-cells you studied in the last experiment.

When two half-cells for different metals were connected by a salt bridge, and a voltmeter was connected between the metal electrode in one half-cell and the one in the other half-cell, you were able to get a reading for the voltage (electrical pressure) between the half-cells. A voltage reading tells us that there is a tendency for electrons to move in the direction from the negative terminal of the voltmeter into the voltmeter and out the positive terminal. The half-cell connected to the negative terminal must be supplying these electrons—there must be an oxidation half-reaction in this half-cell. The electrons travel through the wire, into the voltmeter, out through the other wire, and into the other half-cell.



**FIGURE F** Oxidation-reduction reaction when a zinc half-cell is connected to an iron half-cell.

There a reduction half-reaction takes place. Positive ions in the solution react with electrons on the surface of the electrode and become neutral atoms.

One combination you studied was zinc in a zinc nitrate solution paired with iron in an iron(III) chloride solution. As you probably discovered, the voltmeter gave a reading when its negative terminal was connected to the zinc half-cell and its positive terminal to the iron half-cell. So we know that oxidation took place in the zinc half-cell and reduction in the iron half-cell. The oxidation produced additional  $\text{Zn}^{2+}$  ions, which entered the  $\text{Zn}(\text{NO}_3)_2$  solution. Now there were more than one  $\text{Zn}^{2+}$  ion for every two  $\text{NO}_3^-$  ions (see Fig. F). The reduction removed  $\text{Fe}^{3+}$  ions from the  $\text{FeCl}_3$  solution. Now there was fewer than one  $\text{Fe}^{3+}$  ion for every three  $\text{Cl}^-$  ions (Fig. F). So there was an excess positive charge in the  $\text{Zn}(\text{NO}_3)_2$  solution and an excess negative charge in the  $\text{FeCl}_3$  solution.

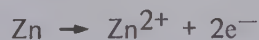
As you might have figured out, the salt bridge helped to restore the charge balance. The sodium sulfate solution in the salt bridge contained negatively charged  $\text{SO}_4^{2-}$  ions and positively charged  $\text{Na}^+$  ions. The negative ions migrated from the wet salt bridge into the oxidation half-cell (zinc, in our example); some of the positive ions in the half-cell (e.g.,  $\text{Zn}^{2+}$ ) migrated into the salt bridge solution. Both these migrations helped to eliminate the excess positive charge.

Similarly, positive  $\text{Na}^+$  ions migrated off the salt bridge into the reduction half-cell (iron, in our example); some of the negative ions in the half-cell (e.g.,  $\text{Cl}^-$ ) migrated into the salt-bridge solution. Both these migrations helped to eliminate the excess negative charge.

While a pair of half-cells will generate a voltage, it is not very convenient to carry around two test tubes filled with solutions whenever you need a voltage. Something more practical had to be invented--and was. Let's take a look at some of these practical inventions.

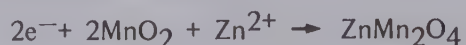
### The Leclanche Cell

Figure G shows a cutaway sketch of the ordinary *dry cell*, or *Leclanche cell* (in honor of the man who invented it). Generally today these dry cells are wrapped with paper, plastic, or thin metal, inside of which is a cup made of zinc, in the shape of the dry cell. The zinc is oxidized when the cell is operating:



The reduction half-reaction is more complicated. Leclanche himself did not know what was happening. In the zinc cup, next to the metal, is a layer all the way around of solid ammonium chloride and zinc chloride mixed with water. Starch is added too, so that the mixture is pasty--not dry but not too loose and wet either. Inside that layer is another mixture, also wet, of grains of manganese dioxide and carbon. And right in the middle is a carbon electrode. If you take a dry cell apart, you will see a black mixture around the carbon electrode, surrounded by a white mixture, with a zinc cup on the outside. The zinc is protected by a paper or other wrapper on the very outside. The top, above the mixture, is sealed to keep the contents in. Below the seal and above the contents is an air space for expansion, since the contents swell a little as the cell is used.

The reduction half-reaction takes place in the black mixture around the carbon electrode. Here is the half-equation:





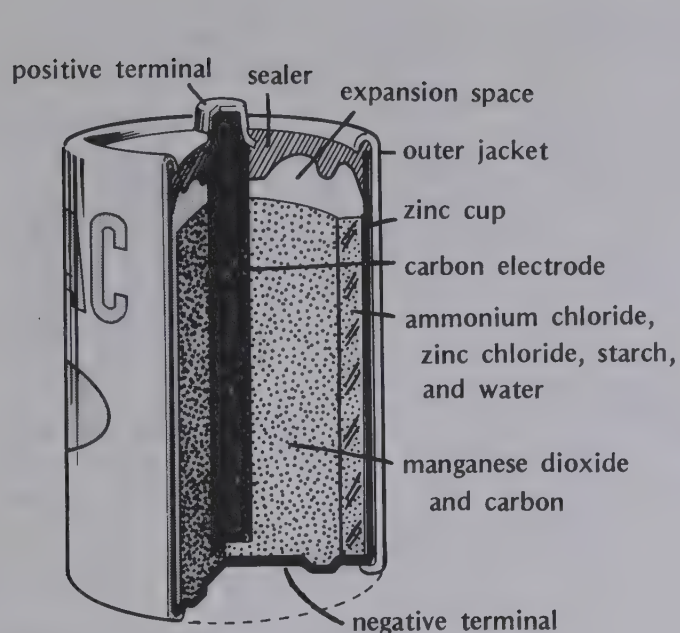


FIGURE G A dry cell, or Leclanche cell.

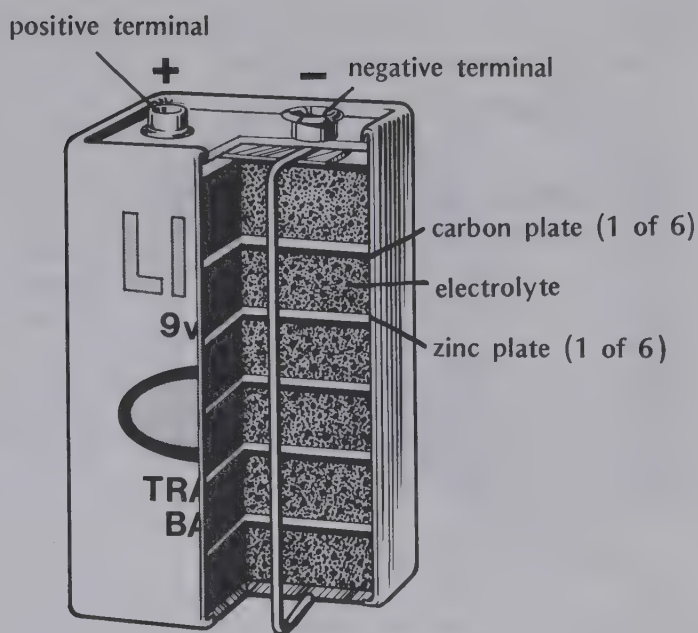
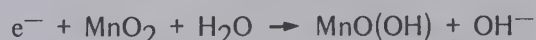


FIGURE H A 9-volt transistor battery.

However, this half equation applies only when the cell is used to produce a small current. One of the advantages of the Leclanche dry cell is its ability to produce a large or a small current. When a large current is needed, a different half-equation applies:



For an intermediate amount of current, probably both of these half-reactions account for the reduction part of the process.

Still other reactions, not mentioned here, also occur. The full details of the working of a Leclanche dry cell are not all understood. A few years ago, for example, it was thought that the manganese dioxide was a "depolarizer" (whatever that is) but now we know that it takes part in the reduction half-reaction.

### Transistor Batteries

You are perhaps familiar with 9-volt *transistor batteries*. These are made of six small Leclanche cells of 1.5 volts each connected in series (side by side) to make the 9 volts. In these batteries (the word *battery* means more than one cell) the Leclanche cells are often made on a flat form, like a little sandwich, one piled on top of another, as shown in Fig. H.

### Mercury Cells

Tiny cells called *mercury cells* are used in watches, photographic light meters, hearing aids, and other devices requiring a compact source of electrical power. A typical mercury cell is shown in Fig. I; it is usually about the same size as a small bean.

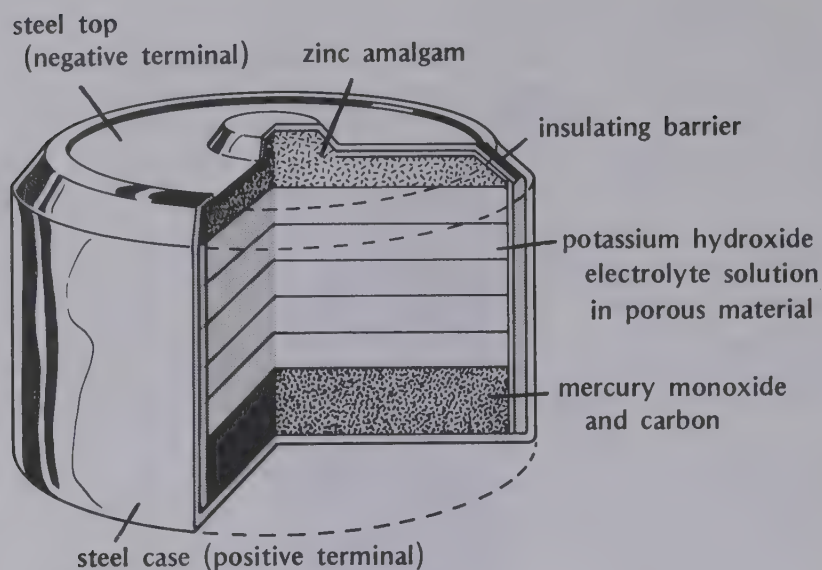
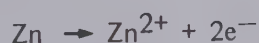


FIGURE I A mercury cell.

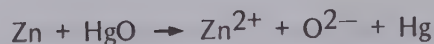
The oxidation half-equation is:



The reduction half-equation is:



The complete equation is:



But inside the mercury cell, the zinc and oxide ions combine to form solid zinc oxide, so the real complete equation is:



Some relatively unimportant secondary reactions produce hydrogen gas, so the cell case must be vented to allow for release of the gas. Also, after this cell is exhausted, or even after it has been used only a little, it contains metallic mercury, which is very poisonous. Metallic mercury evaporates, and it is harmful to breathe its vapor. So do not ever put a used or partially used mercury cell in a fire to dispose of it. The mercury vapor that would be released in such a case could cause serious harm. Never take a mercury cell apart except under close supervision by someone who knows how to protect you, and others, from poisonous mercury.

### Rechargeable Cells: The Nickel-Cadmium Cell

What about rechargeable cells and batteries? Several different kinds are in use today, for different purposes. One of these is the *nickel-cadmium cell*. It can

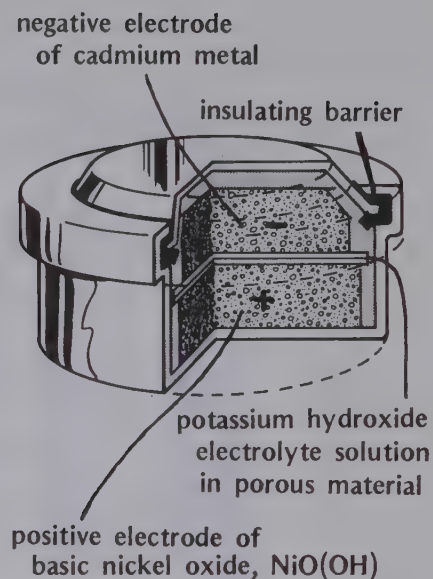


FIGURE J A nickel-cadmium cell.



be made in a relatively small size and in almost any shape, and does not require venting. Thus it has many safe uses in the home and laboratory. Fig. J shows the general construction.

The oxidation half-reaction involves cadmium instead of zinc. As a chemistry student, you might have suggested this if you were to design a new cell. You know that zinc is used in some cells, therefore cadmium which is in the same family on the periodic table as zinc, might also be predicted to be usable in a cell.

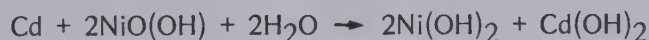


The reduction half-reaction is somewhat similar to the reduction half-reaction in the Leclanche cell. Again, this is a reasonable prediction since nickel and manganese are both elements with only partially filled  $3d$  orbitals and with outer, filled  $4s$  orbitals.

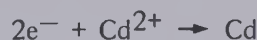


Perhaps with the help of the periodic table you could think of another combination of possible half-reactions that could be used to make a new kind of cell.

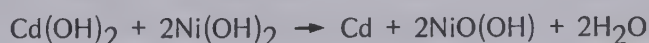
When the nickel-cadmium cell is discharged, the products inside the cell are nickel hydroxide and cadmium hydroxide, as you can see from the overall equation:



By applying an external voltage higher than the voltage developed by the cell itself, we can reverse the half-reduction and half-oxidation reactions:



In this case, the overall reaction consumes the two hydroxides and forms the original cadmium and basic nickel oxide, and water:



This is called “charging the cell”; all it really does is to reverse the cell’s half-reactions and restore the original materials so that the cell can be used once again. The charging can be repeated several times, as you know.

### Rechargeable Batteries: The Lead-Acid Storage Battery

Automobiles require a source of electrical energy that will produce a great number of electrons flowing per second—that is, a high-current source. The most common, practical high-current source made from cells is the *lead-acid storage battery*. It has three or six cells, depending on whether it is a 6-volt or 12-volt battery.

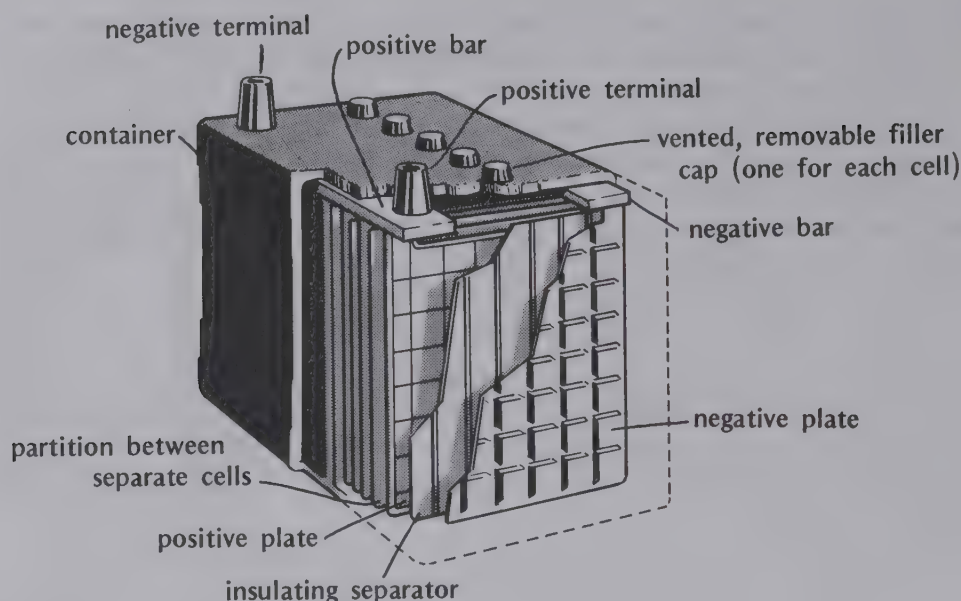
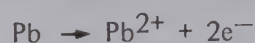


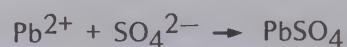
FIGURE K A lead-acid storage battery.

Each cell generates 2 volts and is separated from the others by compartments. You may have noticed that the storage battery in an automobile has either three or six caps. Each cap leads to one cell. The cap can be removed to replace water lost by evaporation or from "overcharging."

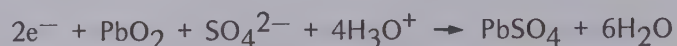
Fig. K shows a view of the construction of a typical lead-acid storage battery. In each cell there are several lead plates. Half are coated, or filled, with lead(II) sulfate and half with lead(IV) oxide. During discharge, the lead plates with the lead(II) sulfate are oxidized:



The lead ions react with sulfate ions in the sulfuric acid solution in the battery. Together, these two ions form a solid precipitate, lead sulfate:

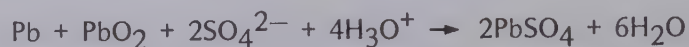


The sulfate ions are also involved in the reduction half-reaction, in which the lead in the lead(IV) oxide-coated plates is reduced (its oxidation number changes from +4 to +2):



Notice that solid lead sulfate is formed in the reduction half-reaction, as well as the oxidation half-reaction. It deposits on the plates in both cases.

We can add all three equations to get the over-all effect of the reaction:

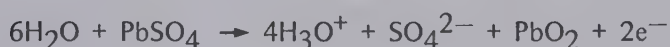


We can see that sulfuric acid (the sulfate ions and the hydronium ions) is consumed in the reaction and solid lead sulfate and water are produced.



You can tell by careful inspection whether a lead-acid storage battery is discharged or not by examining all the plates. If they look alike—that is, if lead sulfate is present on both kinds—the battery is discharged. An easier way to tell is to measure the density of the solution in each cell. As the battery is discharged, sulfuric acid is consumed in each cell and water is formed. Sulfuric acid solutions have a higher density than water. So, as the cells are discharged, the density of the solution decreases. A fully charged storage battery solution has a density of 1.280 g/cc. When the cells are practically completely discharged, the density is about 1.200 or 1.100 g/cc. An absolutely discharged battery solution has a density of less than 1.100 g/cc, and probably cannot be recharged.

When the battery is recharged, the same half-reactions take place, but in reverse:



Notice that in the charging half-equations, sulfuric acid—that is, hydronium ions and sulfate ions—are formed. So as a battery is charged, you can check the density of the solution in each cell. When the density reaches 1.280 g/cc, the battery is fully charged.

If you wish, you can make your own lead-acid storage cell. Begin with two pieces of sheet lead, perhaps a few centimeters long and wide and a few millimeters thick. With a sharp instrument, such as an ice pick, make many indentations in the surface of both lead sheets. Rub a paste of wet lead(IV) oxide into the indentations of one sheet and a paste of wet lead(II) sulfate into the indentations of the other. Partially immerse both, not touching, in a sulfuric acid solution whose density is about 1.2 to 1.3 g/cc.

As your experimental cell is used, you will notice that the solid lead(IV) oxide which you worked into the indentations of one sheet changes its appearance, and more solid also forms in the indentations of the other sheet. As the cell is used, you may notice that the solids in the indentations of both sheets have a somewhat similar appearance. You will also notice that the density of the electrolyte solution is less. Your cell can be recharged by using a direct-current source with a voltage slightly more than 2 volts, if you attach the wires from this source to the proper electrodes of your now partially discharged experimental cell. Study the half-equations given for the recharging process, to see which wires to attach to which electrodes.

## REDOX EXPERIMENT 5 • CORROSION

We have applied what we have learned to cells, and learned how Leclanche cells, storage batteries, and other similar devices work. Next, let us apply this knowledge to a related field, the corrosion of metals.

### Purpose:

To learn more about the relation between oxidation-reduction reactions and corrosion.

**Materials:**

1.5 grams agar  
100 cc water  
1 250-cc beaker  
2 cc 0.05% alcoholic phenolphthalein solution  
6 cc 1% water solution of  $K_3Fe(CN)_6$   
5 cc 3M NaOH solution  
5 cc 3M  $HNO_3$  solution  
1 watch glass, 75 mm  
20-cm x 20-cm cloth (for filter)  
1 iron nail  
1 stirring rod  
emery cloth  
pair of pliers

**Procedure:****PART I: PREPARING THE AGAR MIXTURE**

1. Put 1.5 grams of agar in the 250-cc beaker and add 100 cc of water.
2. Heat to boiling, stirring occasionally. Boil gently for about 45 minutes, or until the agar is dispersed in the hot water.
3. Filter the agar mixture through a cloth. Discard any substance remaining on the cloth.
4. Add 2 cc of phenolphthalein solution to the hot agar mixture.
5. Then add 6 cc of the potassium ferricyanide solution. Stir the mixture well to thoroughly mix all ingredients.
6. Stirring all the time, add a few drops of the sodium hydroxide solution *slowly*, drop by drop, until the hot agar solution just barely turns pink.
7. Add a very few drops (not more than 2 or 3) of the nitric acid solution, stirring all the while, until the pink color barely disappears. If too much nitric acid is added, then add a bit more sodium hydroxide solution and after that a drop or two of nitric acid until the pink just barely disappears.
8. Pour about half of this hot mixture into the watch glass to cool and gel. Keep the remainder of the agar mixture hot.

**PART II: LETTING THE NAIL REACT**

1. Clean the iron nail with the emery cloth and rinse well.
2. Bend the nail into a "V" shape with as acute a bend as you can manage.
3. Gently embed the bent nail in the cooled, set agar gel.
4. Pour the remaining hot agar mixture on top of the nail in the set agar gel; be sure to cover the nail completely.
5. Let the entire system cool to room temperature. Observe it as often as possible for the next several hours. Within a few hours (or sooner) you will notice some changes. It is interesting to watch these changes begin and grow in extent. Keep a record of all observations.
6. If you wish to keep the agar gel for several days, it must be preserved



against mold by storing it in a closed container with alcohol vapor. Place it in a dessicator with a little alcohol in the bottom chamber. Rubbing alcohol, wood alcohol, or grain alcohol may be used.

7. Clean all equipment and return to its proper place.

### Questions:

1. Describe the changes that took place after you put the nail in the agar gel. If you are able, illustrate with neat sketches.
2. The blue color indicated the presence of  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ , which is used to produce some blue inks. It is produced when iron from the nail is oxidized to iron(II) ions, and these ions then react with  $\text{Fe}(\text{CN})_6^{3-}$  ions from the potassium ferricyanide solution. Write balanced half-equations and equations for (a) the oxidation half-reaction; (b) the formation of  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ .
3. The pink color indicated that there were  $\text{OH}^-$  ions in the presence of phenolphthalein solution. The  $\text{OH}^-$  ions were produced when electrons given off during the oxidation of the iron reacted with water molecules to form hydrogen gas and hydroxide ions.
  - a. Write a balanced half-equation for this half-reaction.
  - b. What is reduced in this half-reaction?
4. What were the electrodes in these half-reactions? (Hint: Where did the oxidation half-reaction take place? Where did the reduction half-reaction take place? )
5. Which reaction (or half-reaction), do you think, represents corrosion? Why did you choose this one?

## REDOX EXPERIMENT 6 • PREVENTING CORROSION

Generally speaking, corrosion is undesirable. One way to prevent corrosion of iron is to place the iron against another metal which is more easily oxidized than iron, even when the iron has been bent or cut. From your work with Redox Experiment 3 or 4, you can guess that such a metal would be zinc. Zinc is used to protect iron from corrosion; the process is called *galvanizing* (you probably have heard of galvanized iron). The next experiment shows how it works.

### Purpose:

To learn how corrosion processes can be prevented by allowing another metal to be oxidized instead.

### Materials:

- 1.5 grams agar
- 100 cc water
- 1 250-cc beaker
- 2 cc 0.05% alcoholic phenolphthalein solution
- 6 cc 1% water solution of  $\text{K}_3\text{Fe}(\text{CN})_6$

- 5 cc 3M NaOH solution
- 5 cc 3M HNO<sub>3</sub> solution
- 1 watch glass
- 3 iron nails
- 1 narrow strip of zinc, 0.5 cm x 2 cm
- 1 flowerpot with moist dirt

### Procedure:

1. Prepare about 100 cc of the same agar gel mixture you prepared in the last experiment, following the procedure in Part I of that experiment. Pour half of the hot mixture into the watch glass and allow to cool and gel. Keep the remaining mixture hot.
2. Using a bent or unbent nail, as you prefer, wrap a narrow strip of zinc around the nail as shown in Fig. L.
3. Embed the nail and zinc strip together in the gelled half of your mixture in the watch glass, and pour the rest of the hot mixture on top. Let the whole thing cool. Observe reactions carefully and record them. Note the presence of only red color around the nail. This indicates that no iron is being oxidized. The white precipitate that you see near the zinc is caused by the reaction of zinc ions with ferricyanide ions to form solid, white zinc ferricyanide, Zn<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>, or zinc di-hexacyanoferrate.
4. Vary this experiment in the following way. Bend one nail into a "V" shape and bury it in moist dirt inside a flowerpot.
5. Bend another nail similarly, but also wrap a zinc strip tightly around it as in Step 2. Bury it near the first nail. After a few days, uncover both nails and note their condition. Record your observations.

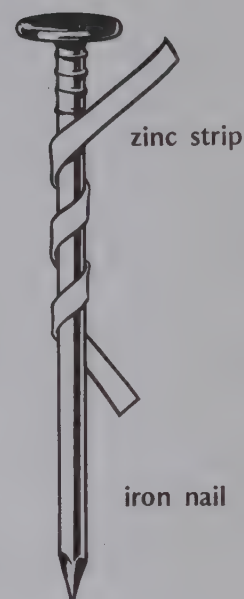


FIGURE L

### Conclusions:

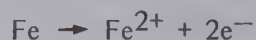
1. Write a description telling how the zinc prevented the corrosion of iron. Use one or more half-equations or complete equations as part of your description.
2. How might the periodic table of electronegativities (Chapter 7 of *Keys to Chemistry*) help you suggest other metals which also might be used to prevent the oxidation of iron by their own "sacrificial" oxidation instead? Use this table to predict some suitable metals to use instead of zinc.

### Suggestions for Further Work:

You may wish to test your prediction about suitable sacrificial iron-corrosion-preventers. If so, prepare a description of the laboratory work you would perform and a list of needed materials, and with your teacher's permission, carry out the investigation.

## REDOX SECTION 8 • CORROSION AND CORROSION PREVENTION

Iron rust starts with this half-reaction:





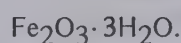
The electrons go off elsewhere and reduce water, or participate in some other reduction half-reaction. The iron ions react with hydroxide ions, which are always present to some extent if water is around, as in moist dirt.



Then, the iron(II) hydroxide reacts with water and with oxygen, which is dissolved in the water, to produce iron(III) hydroxide:



Iron(III) hydroxide,  $\text{Fe}(\text{OH})_3$ , is rust. Some people prefer to write the compound in a different form:



### Rust Prevention

One way to prevent iron from rusting or corroding is to cause some other metal to take part in the oxidation half-reaction instead of iron. Zinc serves this purpose very well, as you saw in Redox Experiment 6.

Another way to prevent iron from rusting is to paint it. You might like to cover an iron nail very thoroughly with paint, and test this with the agar gel mixture. If your paint does prevent oxidation of the iron, perhaps you would like to nick the paint coating in a couple of places, and then test it again with the agar gel mixture.

A third way to prevent iron from rusting, or oxidizing, is to cover it with another metal, but one which is *less* easily oxidized. Tin is suitable. In fact, most tin cans are cans made of iron, coated on the outside with a thin layer of tin and on the inside with a layer of varnish or plastic. The tin protects the iron from oxidation just as paint does. But if the tin layer is nicked or cut, the iron is oxidized and the tin acts as the other electrode, just the opposite of the case with zinc and iron. You might try nicking a piece of a tin can, thus exposing the iron underneath, and put it in some agar gel mixture to see what happens.

Would copper prevent iron from corroding? One way to test this is to wrap an iron nail partially with a piece of copper wire and embed the whole thing in some agar gel mixture. If you try this, you will get negative results. Under other circumstances, however, copper does, somehow, prevent iron from rusting severely. Today you can see unpainted steel (steel is an alloy of iron, carbon, and other substances) used for bridges and buildings. Even though it is not protected by paint, the steel does not rust further, once a layer of rust has formed. These special "non-rusting" steels are called *weathering steels* because they can be exposed to the weather without corroding away to a pile of rust. Weathering steels are alloys in which copper, phosphorus, nickel, chromium, and sometimes silicon are added to the basic alloy of iron and carbon. When they are exposed without paint or other protection, a tightly adhering layer of rust is formed, but any further rusting is prevented by the layer of rust. Although steel scientists have been studying this phenomenon for several years, no one has yet been able to explain why it happens.

This is a good example of the point that science cannot explain all things, even when many scientists try to do so. Meanwhile, everyone can enjoy what cannot be explained. For example, the abstract statue by the late Pablo Picasso, located in the Chicago Civic Center Plaza, is made from weathering steel. As you can see from the photograph (Fig. M), some people have trouble explaining it, too! (Other people who are more sensitive to fine works of art like it very much, mostly because it is a happy, joyful expression of the artist's feelings.)

### Practical Considerations

Why do builders consider it bad practice to use iron nails to fasten aluminum gutters on houses? (They usually use aluminum nails instead.) One way to find out is to pierce a small piece of aluminum foil with an iron nail, and put the whole thing in the agar gel mixture.

In general, when two different metals are exposed to the weather, one is more easily oxidized--more readily corroded--than the other. After exposure of a few weeks, months, or years, one of the two metals, the more easily oxidized one, is partially or completely gone, corroded away. In a plumbing installation, for example, it is bad practice to attach an iron pipe to a copper pipe, unless the joint is separated by an electrical insulator to prevent electrons from going from the oxidation half-cell to the reduction half-cell. Copper flashing on a roof should be fastened with copper nails, not some other metal. Aluminum screening should be fixed to the screen frame with aluminum staples or tacks, not steel fasteners.

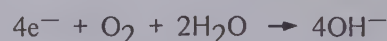
### Corroding Car Bodies

Another example of a common corrosion problem is the corrosion of car bodies. If a car is dented or nicked, exposing the car body to the air, rust will form on these bare spots. If nothing is done to stop it, the corrosion will spread *under the paint*. You would think that the paint would protect the iron underneath from corroding, but it seems as though the paint encourages the corrosion instead of preventing it! This is correct; once the protective paint cover is broken, the paint that is left actually encourages more corrosion underneath. (The best practical way to stop it is to paint over the broken paint seal immediately, making very sure that no holes exist in the paint patch.)

Figure N shows how paint promotes corrosion of iron, once the paint seal is broken through. At the spot where the paint is broken, iron can be oxidized (1). All we need is a little water, in which the iron ions can dissolve.



If that water contains dissolved oxygen, and most water produced naturally does, then the mixture of oxygen and water is reduced by the electrons released from the oxidation of the iron, and hydroxide ions are produced (2).

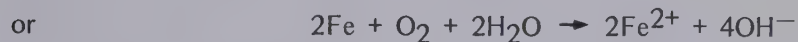
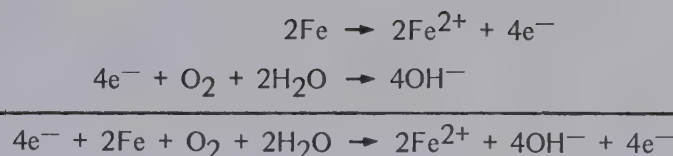


The complete equation is:



FIGURE M Picasso metal sculpture of weathering steel. (Courtesy American Iron and Steel Institute)





The oxidation half-reaction can take place anywhere the iron metal is exposed to a little water, but the reduction half-reaction can take place only where both oxygen and water are available, along with the necessary electrons.

The two half-reactions cannot take place at exactly the same location; they must be separated in space at least a little bit. As the reduction half-reaction occurs, oxygen in the water is consumed, and more oxygen from the air dissolves in the water. But that newly dissolved oxygen is more likely to get near the



FIGURE N How paint promotes the corrosion of iron.

metal in the center of the exposed metal spot. That is, most of the newly dissolved oxygen would pass near the center before it got to the edges. Or, to say it differently, there is less oxygen available at the edges of the exposed metal and more oxygen available in the center of the exposed metal. So, the reduction half-reaction tends to take place in the center of the exposed metal. The oxidation half-reaction tends to take place elsewhere, at the edges of the exposed metal (3). Eventually, the iron at the edges, and underneath the paint, is oxidized and corrodes away. The iron in the center does not corrode as much (4).

Actually, once in a while the iron in the center is oxidized away also. The  $\text{Fe}^{2+}$  ions react with the  $\text{OH}^-$  ions to form  $\text{Fe}(\text{OH})_2$ , and this reacts further with oxygen and water to form rust, as we have already learned.

## REDOX EXPERIMENT 7 • TAKING WATER APART

Most of the oxidation and reduction half-reactions we have looked at thus far were spontaneous. Other oxidation and reduction half-reactions can be forced to happen. We have already seen one example of the forced oxidation and reduction of water. In Part II of Redox Experiment 1, the spontaneous oxidation-reduction involving magnesium atoms and copper ions forced the oxidation and reduction of water in the wet strip of pH test paper.

The forced oxidation and reduction of water is also called *electrolysis* of water. The word *electrolysis* can be understood by taking it apart. The first seven letters, *electro-*, remind us of *electrons*. The last five letters are from the Greek word for breaking up, or coming apart. So, as you can guess, the word *electrolysis* means "taking apart by using electrons."

### Purpose:

To enjoy the electrolysis of water.

### Materials:

1 gram ammonium chloride  
100 cc water  
phenolphthalein solution  
stirring rod  
9-volt transistor battery  
250-cc beaker

### Procedure:

1. Dissolve 1 gram of ammonium chloride in 100 cc of water in a 250-cc beaker.
2. Immerse the 9-volt transistor battery in the solution. Observe the results and record your observations.



3. Remove the battery and add 2 to 3 drops of phenolphthalein solution to the ammonium chloride solution while stirring.
4. Immerse the battery in the solution again. Record your observations.

### Questions:

1. Do you think that water could be electrolyzed by using some kind of electrical source other than a 9-volt transistor battery? Or do you think that this would not be possible? Explain the reasons you have for your prediction.  
 WARNING: Some students have predicted that water could be electrolyzed by using the 115-volt source of alternating current generally available in ordinary electrical outlets. Then without proper permission, they tested their prediction. In some cases (we are not saying whether their prediction about electrolyzing water was correct or incorrect), the results were most unpleasant. That is, 115 volts of electrical pressure is enough to be fatal, in some cases, depending upon the details of the situation. Whatever the details might be, 115 volts is almost always enough to be joltingly painful.
2. If the ammonium chloride were replaced by one of the following solutes: (1) salt, (2) baking soda, (3) sugar, (4) potassium iodide, would the electrolysis of water take place? Test your predictions by repeating the experiment for these solutes.

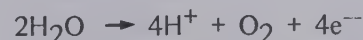
## REDOX SECTION 9 • THE OXIDATION AND REDUCTION OF WATER

At one terminal of the battery, where electrons are released from oxidation-reduction reactions that take place inside the battery, water is reduced:

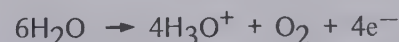


According to this half-equation, for each two moles of electrons from the battery, one mole of hydrogen molecules is formed, along with two moles of hydroxide ions.

At the other terminal of the battery, where electrons are taken in, water molecules are oxidized:



The hydrogen ions,  $H^+$ , become attached to other water molecules to form hydronium ions,  $H_3O^+$ . So a better half-equation can be written like this:



Either half-equation tells us that for each four moles of electrons given up to the battery terminal, one mole of oxygen molecules is formed.

In the complete reaction, the hydroxide and hydronium ions recombine, and the complete equation is simply



as you first learned in Redox Section 4.

### The Indicator Color Change

At the battery terminal marked with a negative sign, the phenolphthalein indicator turns the solution pink, indicating the presence of  $\text{OH}^-$  ions. Thus, this must be the terminal that releases electrons, causing water molecules to be reduced. The bubbles that can be seen must be gaseous hydrogen.

At the other terminal, the solution does not turn color. Thus, this must be the terminal at which water molecules are oxidized, and the bubbles that can be seen must be gaseous oxygen. Did you observe that there were more or bigger bubbles of hydrogen than of oxygen? This is predicted by the complete equation.

You may have tried variations on this experiment using other solutes—salt, baking soda, sugar, or potassium iodide—in place of ammonium chloride. Potassium iodide is a particularly interesting solute. When it is used, the iodide ions in the solution are more easily oxidized than water is, so iodine is formed as well as a few bubbles of oxygen gas at the terminal where oxidation takes place. The iodine dissolves in the water, forming a colored solution around the region of the battery terminal.

It is reasonable to use other indicators, instead of phenolphthalein. Some indicators turn one color in the presence of hydroxide ions and another color in the presence of hydronium ions. So you can make a two-colored solution by selecting the proper indicator.

### Summary

A brief summary will be helpful at this point. The reactions that you studied in the first part of this module were spontaneous oxidation-reduction reactions. All we had to do was to put two or more substances together, and one was oxidized while the other was reduced. One substance gave up electrons and the other took them. But in the work with the ammonium chloride solution the oxidation and reduction did not happen until we added a source of electrons (the negative terminal of the battery) and added a place for electrons to go (the positive terminal of the battery). Actually, we did not really have to use any solute dissolved in the water. The presence of the ammonium ions and of the chloride ions merely facilitated the oxidation and the reduction, making it go much, much faster. If no solute were dissolved, the rate of bubble production of hydrogen and oxygen gas would be much slower, so slow that some people probably wouldn't notice any bubbles.

As you probably remember from your study of Chapter 4 in the text, ammonium chloride is an electrolyte. That is, in solution it promotes the taking of electrons from one terminal of the battery and the return of electrons to the other terminal. If you used salt, baking soda, or potassium iodide as a variation of the experiment, you noticed that all of these are also electrolytes, whereas sugar is a non-electrolyte.



## REDOX EXPERIMENT 8 • THE COPPER PENCIL

We can try some additional examples of forced oxidation-reduction reactions, in which we supply the source of electrons and a place for them to go to.

### Purpose:

To observe the reduction of copper ions and the formation of a coating of copper atoms on a pencil point.

### Materials:

- 1 soft graphite pencil (a carpenter's pencil is ideal for this experiment since it contains a quite large, soft clay-graphite core)
- 9-volt transistor battery
- 25 cc 1M  $\text{CuSO}_4$  solution
- 50-cc beaker
- 10-cm copper wire, not insulated
- 4 alligator clips
- 2 20-cm pieces of insulated copper wire with about 1 cm of insulation removed from each end

### Procedure:

1. Sharpen both ends of the pencil.
2. Pour 25 cc of 1M copper(II) sulfate solution into the beaker.
3. Bend the noninsulated copper wire into the shape of the letter "J." Turn

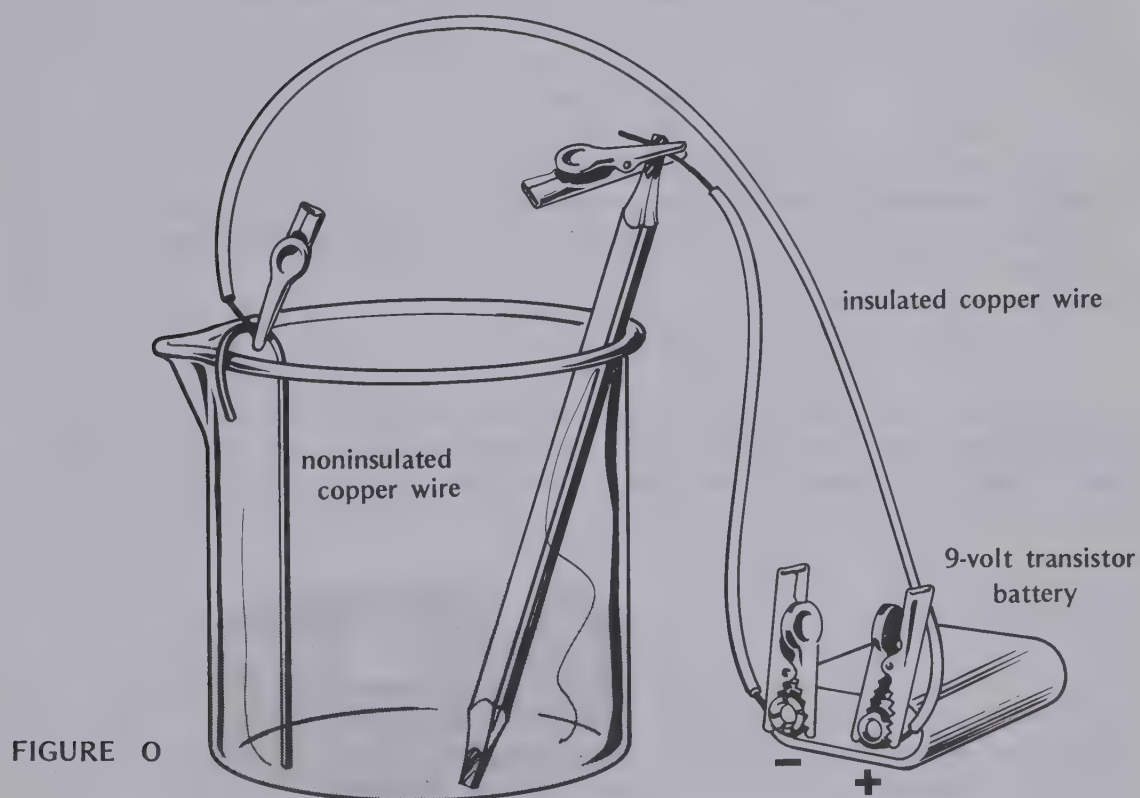


FIGURE 8

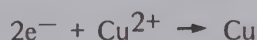
- it upside down and hook the curved end over the edge of the beaker. The other end should be long enough to dip into the copper sulfate solution.
4. With two alligator clips and a short length of insulated copper wire, attach the upper end of the "J"-shaped copper wire to the positive terminal of a 9-volt transistor battery. Using a second pair of alligator clips and a short length of insulated copper wire, attach one end of the double-ended pencil to the negative terminal of the battery. NOTE: Be *sure* that the alligator clip is in firm contact with the graphite (pencil "lead").
  5. Dip the other end of the pencil into the copper(II) sulfate solution, making certain NOT to touch the copper wire that is in the beaker. See Fig. O.
  6. Leave the pencil in the copper(II) sulfate solution for a few seconds, then withdraw it and examine the wet end closely. Record your observations. You may dip the pencil in the solution again for a longer period of time.

### Questions:

What would happen, do you think, if the connections to the battery were reversed? Account for your prediction by using your knowledge of oxidation and reduction processes.

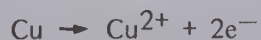
## REDOX SECTION 10 • ELECTROPLATING COPPER AND SILVER

In the last experiment, copper(II) ions in the copper(II) sulfate solution were reduced at the graphite pencil electrode when they reacted with electrons that entered the graphite from the negative terminal of the battery:



The copper metal atoms formed on the surface of the black graphite, giving it a reddish appearance. You electroplated copper onto graphite.

At the other electrode, the "J"-shaped copper wire, an oxidation half-reaction took place:



These electrons traveled back into the battery through the positive terminal. Overall, copper atoms were oxidized to ions and copper ions were reduced to atoms. Copper atoms were removed from the wire and put in solution, and just as many copper ions were removed from solution and put on the graphite.

### Counting Electrons

Notice that this is a way to count electrons! We can see from either half-reaction that for each mole of copper, two moles of electrons are involved. So, by weighing the copper wire before and after, and calculating the loss in weight, we could figure out how many moles of copper atoms were oxidized. Then twice

that many moles of electrons would have been given up by the negative terminal of the battery.

Also, we could have weighed the pencil before and after (being sure that it is dry before weighing it the second time) and calculated the gain in weight due to the copper atoms that were electroplated on it. That many moles of copper atoms, then, multiplied by two, would be the number of moles of electrons given back to the battery through its positive terminal.

As you may have guessed, very careful scientific workers have proved that the number of moles of copper atoms lost at one electrode is exactly the same as the number of moles of copper atoms gained at the other electrode. Michael Faraday, whom you read about in Chapters 3 and 4 in the text, was one of the scientists to study this very thoroughly. In his honor, statements about the number of moles of atoms that are oxidized (or of ions that are reduced) and the number of moles of electrons that are also involved are known as "Faraday's Laws of Electrolysis."

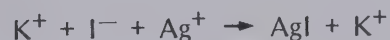
Did you ever see a copper dime? Now that you know how to electroplate copper onto graphite, you can also electroplate other substances with copper. Remember, the more moles of electrons that leave and re-enter the battery, the more moles of copper you can electroplate. A thin coating of copper is soon rubbed off; a thicker coating takes longer to deposit but also lasts longer.

### Electroplating Silver

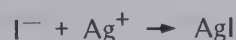
How about a silver penny? It is possible to electroplate silver onto various substances also. In principle, all we need is to have some silver ions in solution, and to reduce them at the electrode connected to the negative terminal. This electrode will become electroplated with silver.

However, it is not quite this simple in practice if you want to get a nice shiny silver coating. The problem is with the concentration of the silver ions in solution. Unless their concentration is very low, the reduction of the silver ions and the formation of the silver coating will take place very rapidly. Silver coatings that are formed rapidly by electroplating do not stick very well and are not very shiny. To make the coating form slowly we must use a very, very low concentration of silver ions in solution. Now, the trouble is that with a very low concentration, soon all the silver ions in solution will be reduced and the coating on the negative electrode will be so thin that you could hardly see it.

The trick is to put the silver ions in solution at a higher concentration to start with, and then tie them up *almost* completely with another ion, in a dynamic equilibrium situation. To do this we add iodide ions, in the form of potassium iodide. When potassium iodide is first added to a solution containing silver ions at a high concentration, a yellow precipitate forms. It is silver iodide.

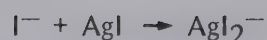


As you can see, the iodide ions react but the potassium ions are spectators, so we might just as well write the equation like this:

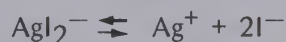


Now, if we add still more iodide ions, a further reaction occurs:





The yellow solid, silver iodide, disappears; it dissolves as more and more of it reacts with the iodide ions to form silver diiodide ions,  $\text{AgI}_2^-$ . In solution, these silver diiodide ions are in dynamic equilibrium with silver ions and iodide ions, at a very, very low concentration:



This is just what we want, silver ions at a low concentration. Besides, notice what Le Chatelier's Principle predicts. As those low-concentration silver ions are reduced to silver atoms by electroplating at the negative electrode, the dynamic equilibrium is disturbed, and more silver diiodide ions will break up, to form more silver ions (and iodide ions), still at a low concentration. So, by this trick, we can have plenty of silver present in solution, tied up with the iodide ions as silver diiodide ions, which will then give us the silver ions we need for electroplating at a low concentration.

## REDOX EXPERIMENT 9 • THE SILVER PENNY

### Purpose:

1. To prepare a solution containing silver ions at a very low and controlled concentration.
2. To use this solution in order to electroplate silver on a cathode.

### Materials:

25 cc 0.5M  $\text{AgNO}_3$  solution  
10 cc saturated KI solution (about 15 grams will dissolve in 10 cc of water, depending on temperature)  
50-cc beaker  
stirring rod  
1 soft graphite pencil, sharpened at both ends  
1 graphite-rod electrode from a discarded Leclanche cell  
1 penny  
9-volt transistor battery  
2 short lengths of insulated copper wire, with bare wire exposed at each end  
3 alligator clips  
porous cloth bag  
pair of rubber gloves

### Procedure:

1. Pour 25 cc of the silver nitrate solution into the beaker.
2. While stirring, add one or two drops of the potassium iodide solution.  
Record your observations.
3. While stirring continuously, add 1 or 2 more drops of the potassium iodide

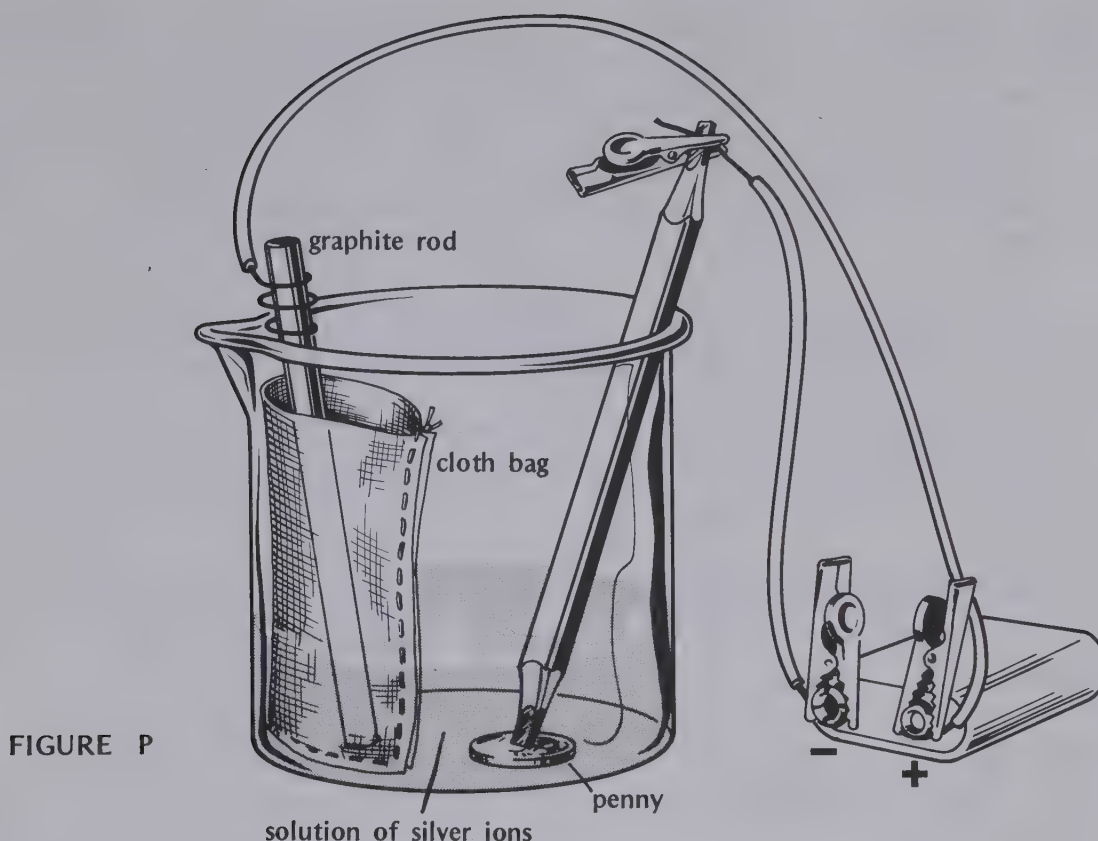


FIGURE P

solution. Then, still stirring, add 1 or 2 drops more. Allow at least 5 minutes between each addition of potassium iodide solution, stirring all the while. (If you want to rest, OK, but don't count resting time as part of the 5 minutes between drops--count stirring time only.) Eventually, one drop will have caused all the yellow precipitate to dissolve. When this happens, you are ready to electroplate.

4. Clean the penny very thoroughly. Use soap or detergent and water--and even a bit of scouring powder. Rinse well when the cleaning has been completed. Wear gloves when handling the penny; otherwise, grease from the skin may interfere with obtaining a really nice electroplated coating.
5. Set up the apparatus as shown in Fig. P. The porous cloth bag is needed to confine the iodine that is formed at the graphite-rod electrode and prevent it from interfering with the electroplating at the other electrode. Notice that the lower point of the double-pointed pencil rests against the penny. The graphite in the pencil permits electrons to flow from the battery to the penny. At the point of contact, the silver plating on the penny will probably be poor, so move the pencil point from time to time. Try to maintain a good electrical contact between the pencil point and the penny. Also, the underside of the penny will not be well coated with silver, since it is resting on the bottom of the beaker. So, after one side of the penny is satisfactorily electroplated, turn the penny over and plate the other side.
6. Plan to take a while to get a nice silver coating on the penny. You can interrupt the electroplating at any time and return to it later.

**Questions:**

1. Write equations which illustrate the way in which you obtain a low concentration of silver ions in solution.
2. Apply Le Chatelier's Principle to explain how the equations you wrote for Question 1 show that the concentration of silver ions is maintained at a low value.

**REDOX EXPERIMENT 10 • THE NICKEL EGG**

This is an optional experiment that can be done for fun.

**Purpose:**

To study nickel-plating by making a nickel-coated egg.

**Materials:**

1 raw egg  
plaster of paris or patching plaster  
copper wire  
wire paper clip  
powdered lubricating graphite  
soft watercolor paintbrush  
45 g  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$   
15 g  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$   
8 g boric acid  
500 cc water  
1000-cc beaker  
9-volt transistor battery  
graphite electrode (the center electrode from a discarded Leclanche cell or a soft graphite pencil sharpened at both ends)  
3 alligator clips

**Procedure:**

1. Make a small hole in each end of the raw egg, and blow out the contents. Discard the contents (or save for an omelette).
2. Mix the plaster of paris or patching plaster with some water so that the mixture has a soupy consistency. Fill the empty eggshell with it. Before the mixture sets, straighten one end of the paper clip and insert into the moist plaster. Fasten the other end of the paper clip to a length of copper wire.
3. After the plaster has set, smooth off the bits of plaster at the holes in the shell. Then thoroughly coat the entire surface with the powdered graphite, using the brush. Be sure the coating touches the paper clip.
4. In the beaker dissolve the nickel sulfate, nickel chloride, and boric acid in the 500 cc of water.



5. Immerse the coated egg in this solution, and attach the copper wire to the negative terminal of the battery. The coating on the egg will be one electrode.
6. Attach the other electrode to the positive terminal of the battery, and immerse it in the solution.

**Questions:**

1. Describe what happens to the egg.
2. Describe what happens to the other electrode.
3. In this experiment, what was reduced and what was oxidized?

**REDOX EXPERIMENT 11 • DUPLICATING MEDALS AND BUTTONS**

This is another optional experiment. If you have medals you have won, or buttons with interesting raised designs, you can make duplicates by electroplating.

**Purpose:**

To make a duplicate medal or button and electroplate it with copper, silver, or nickel.

**Materials:**

medal or button to be duplicated  
 paraffin or candle wax  
 powdered lubricating graphite  
 soft watercolor brush  
 copper wire uninsulated  
 graphite electrode (the center electrode from a discarded Leclanche cell or a soft graphite pencil sharpened at both ends)  
 9-volt transistor battery  
 alligator clips  
 copper sulfate solution as in Redox Exp. 8; silver solution prepared as in Redox Exp. 9; or nickel solution prepared as in Redox Exp. 10  
 beaker

**Procedure:**

1. Warm the wax in your hands until it is soft. Press the warm wax firmly on the medal or button so that it covers the surface you want to duplicate.
2. Carefully peel off the wax. Inspect it to be sure that you are satisfied with the impression in the wax. If not, try again.
3. Coat the configured wax surface with powdered graphite, using the brush. Be sure to get a thorough coating, well brushed in.
4. Attach a bare copper wire to the graphite-coated wax so that the wire makes

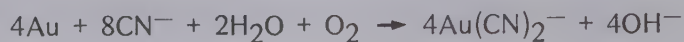
- contact with the graphite. It may be helpful to curve the wire so that it can lie in a circular groove, all around the edge of the design in the wax.
5. Immerse the wax and the attached end of the copper wire in the electroplating solution you have chosen. Complete the circuit, using the other electrode and the battery.
  6. When the wax impression is coated with metal to your satisfaction, melt off the wax.

### Question:

Describe the oxidation-reduction reaction that took place, explaining what was oxidized and what was reduced.

## REDOX SECTION 11 • ELECTROPLATING GOLD

You can even do gold plating in the laboratory. It is expensive, although not prohibitively so. The electroplating solution is prepared by dissolving gold foil in potassium cyanide (KCN) solution. The solution is stirred as the gold foil dissolves; this traps some air bubbles, which are needed in the following reaction:



This is an oxidation-reduction reaction. The gold is oxidized from zero to +1 while the gaseous oxygen (from the air bubbles) is reduced from zero to -2. The gold is now in solution as part of the dicyanoaureate,  $\text{Au}(\text{CN})_2^-$ , ion.

Notice that the potassium ion,  $\text{K}^+$ , is not shown in the previous equation. It is present in the solution only as a spectator ion and does not take part in the reaction, so there is no need to show it in the equation.

If you were working with this solution, you would probably notice an unusual odor when you dissolved the potassium cyanide in the water. This odor is the odor of hydrogen cyanide, HCN, a very poisonous gas. The HCN is produced by an acid-base reaction in the potassium cyanide solution. The cyanide ion,  $\text{CN}^-$ , is a strong base; it will take a proton from water:



As you can see from the double arrow, this is an equilibrium reaction. But as the HCN escapes, as a gas, Le Chatelier's Principle predicts that more HCN will be formed. To prevent the loss of HCN, the solution should be kept in a stoppered bottle when it is not being used.

Potassium cyanide is also used to obtain gold from the earth. Gold often occurs in nature as tiny granules, too small to be handled easily, mixed in with tons of sand and gravel. The sand, gravel, and gold mixture is washed in a solution of potassium cyanide while air is stirred in. The gold is oxidized and forms the dicyanoaureate ion in solution. Then the sand and gravel are filtered off, and acid is added to the solution. This produces more HCN gas, and the gold forms a precipitate in the bottom of the container. The gold can then be filtered out.

## REDOX EXPERIMENT 12 • THE GOLDEN TOUCH

This experiment can be done if time and money allow; it is optional.

### Purpose:

To prepare a gold electroplating solution and to gold-plate an object.

### Materials:

object to be gold-plated (piece of jewelry, coin, etc.)  
piece of gold foil, about 2 cm x 3 cm, or several pieces with a total area of about 6 cm<sup>2</sup> (can be obtained from a local jeweler)  
0.5 g KCN  
100 cc water  
stirring rod  
beaker  
old toothbrush (for scrubbing object)  
soap, detergent, or household ammonia water  
copper wire, uninsulated  
chromel wire  
9-volt transistor battery

### Procedure:

1. Clean the object to be gold-plated well with soap, detergent solution, or household ammonia water. An old toothbrush makes a helpful scrubbing tool. Wear gloves to protect the object from the oils in your skin. After scrubbing it, rinse well. Fasten a piece of bare copper wire to the back of the object, so that it can later be suspended in the electroplating solution.
2. Dissolve the potassium cyanide in the water. Place the gold foil in this solution and stir. CAUTION: Because poisonous hydrogen cyanide gas is produced, this work should be done inside a laboratory hood, or outdoors in the open air. Do not purposely inhale when your nose is close to the solution; if you do so, you may get a headache. If you should happen to inhale some HCN gas, immediately breathe some fresh air, filling your lungs completely several times. Also, the solution you are working with is poisonous. Use newspapers or paper toweling under and around your work, to catch splashed droplets.
3. Suspend the object in the solution containing the dicyanoaurate ions so that the solution covers the area to be plated. Connect the free end of the copper wire to the negative terminal of the battery.
4. Connect the chromel wire to the positive terminal of the battery, and place the other end in the solution, making sure it does not touch the copper wire or the object. For a good gold plating, the process should occur slowly. The farther apart the two electrodes, the slower the process will occur.

### Question:

Describe the reaction in which the object becomes gold-plated, telling what is oxidized and what is reduced.



## REDOX EXPERIMENT 13 • ELECTROETCHING

So far, in our work with electroplating, we have emphasized the reduction half-reaction that takes place at the electrode connected to the negative terminal of the battery. There is an opposite process—called *electroetching*—that involves oxidation at the electrode connected to the positive terminal. This experiment is an illustration of electroetching.

### Materials:

copper wire, uninsulated  
cleaned steel washer, the larger the better  
paraffin or candle wax  
pointed tool, such as a toothpick, pin, or nail  
10 g  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$   
100 cc water  
beaker  
9-volt transistor battery  
clean iron nail

### Procedure:

1. Tightly wrap the end of a piece of copper wire several times around the cleaned steel washer.
2. Melt the paraffin. Dip the entire washer, including the copper wrapping and part of the straight section of the copper wire, into the melted paraffin. Lift it out and let the paraffin coating solidify by cooling. It is important that the washer and copper wire wrapping be completely covered by solid paraffin. It is better, however, if the coating is thin rather than thick.
3. Use the pointed tool to scratch through the paraffin, making a design. For example, you might wish to write your name or the name of a friend. Or you might want to inscribe a religious symbol or flower design if that pleases you. Be sure that you scratch all the way through the paraffin and expose the steel washer. The more care you take with this artistic effort, the more pleased you will be with the final result.
4. Dissolve the nickel sulfate in the water. Immerse the prepared washer in this solution by using the straight end of the copper wire as a handle. Be sure that the paraffin coating on the wire extends above the solution--do not allow the uncoated part of the copper wire to be in the solution.
5. Connect the free end of the copper wire to the positive terminal of the battery. This will allow electrons to be drawn off of iron atoms in the washer. The iron ions formed in this oxidation enter the solution.
6. For the other electrode, wrap another piece of copper wire tightly around a clean iron nail, and connect the free end of the wire to the negative terminal of the battery. Immerse the nail about halfway into the solution.
7. Observe what happens and keep a record of your observations. You will probably see a metal being electroplated on the iron nail. After a while (it may take longer than you would wish), enough iron atoms will have been oxidized wherever you scratched through the paraffin coating to have



FIGURE Q

produced an etched-like incision in the washer. When you think the etching has gone far enough, remove the washer and unwrap the copper wire. Melt off the paraffin coating by dipping the washer in hot, soapy water at a temperature of at least 60° C.

### Questions:

1. Describe the oxidation-reduction reaction that occurred, telling what was oxidized and what was reduced.
2. a. What do you predict would happen if, after you finished etching a design in the steel washer and without melting off the paraffin, you carried out the procedure for copper-plating described in Redox Exp. 8, using the coated washer instead of the double-pointed pencil?  
b. Write half-equations or complete equations, as appropriate, to describe chemically what would happen in the variation of Redox Exp. 8 just described.

### Suggestions for Additional Investigations:

Once you have practiced with designs in the washer, you might wish to electrically etch other metallic objects. Some students have used pieces of tin cans, and have etched their initials or name clear through the thin tin-can metal. Others have etched aluminum sheets, copper sheets, etc. With a bit of artistic skill and patience, it is possible to make some very delightful etchings. Always connect the object to be etched to the positive terminal. You can use any piece of metal, or graphite, as the other electrode. Usually, a 9-volt battery will be a satisfactory electrical source, but you could use a source of direct current with a greater or lesser voltage and note the difference, if any, in the results. You can change the distance in solution between the two electrodes as long as they don't touch each other, and then study the effect of this kind of variation.

Electrical etching is used in industry to make the so-called printed circuit boards used in radios and TV sets. It is used as part of the process in making transistors, in many cases.

## REDOX EXPERIMENT 14 • THE PREPARATION OF LITHIUM METAL

Next, we can consider some other practical applications of oxidation-reduction reactions. All the aluminum metal used in the world, for example, is obtained by the reduction of aluminum from oxidation number +3 to zero at the negative terminal. Figure R shows one example of a cell using this process. Pure aluminum oxide,  $\text{Al}_2\text{O}_3$ , is dissolved in a melted mixture of sodium, calcium, and aluminum fluorides,  $\text{NaF}$ ,  $\text{CaF}_2$ , and  $\text{AlF}_3$ . Large quantities of electricity are needed and as a result, most aluminum refineries are located where the cost of electricity is low.

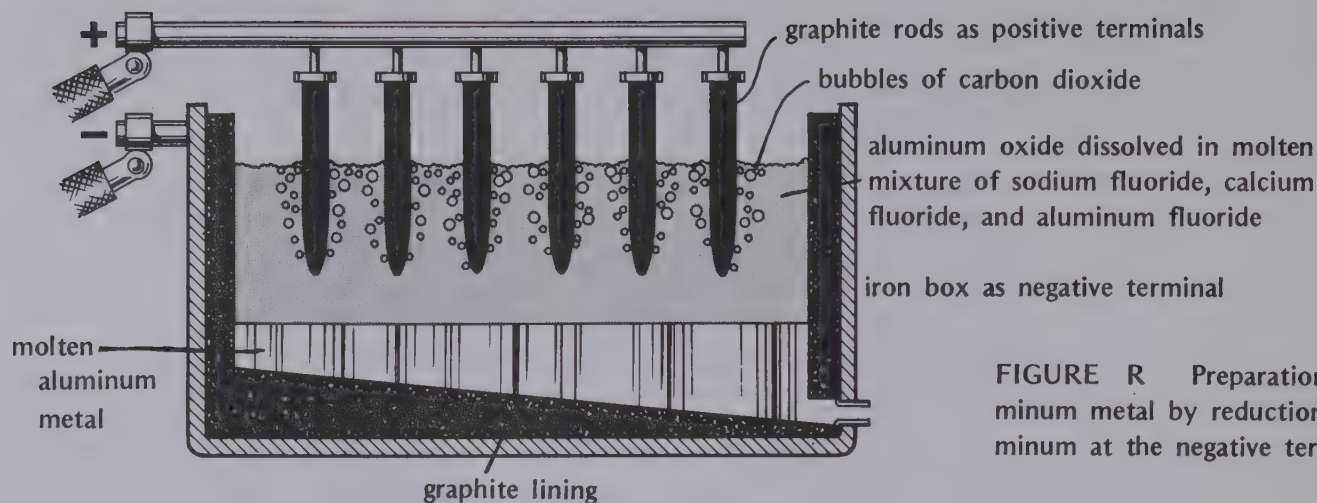


FIGURE R Preparation of aluminum metal by reduction of aluminum at the negative terminal.

We can see how this process works in a general way by preparing some metallic lithium, in this experiment. The method you will use parallels the method of preparing aluminum metal by electrolysis.

### Purpose:

To observe the preparation of a metal, lithium, by the reduction of its ions in a molten salt solution.

### Materials:

piece of iron wire from old coat hanger, about 15 cm long  
 emery cloth  
 1M HCl  
 piece of graphite, 3 to 5 mm in diameter and 4 to 5 cm long (such as a thick pencil lead or the graphite electrode from an old Leclanche cell)  
 soap or detergent solution  
 crucible  
 LiCl  
 ring and ringstand  
 triangle  
 clamps  
 copper wire  
 9-volt transistor battery  
 paraffin (optional)  
 stoppered bottle (optional)

### Procedure:

1. Use emery cloth to remove the paint completely from the iron wire. Then bend one end to form a loop, or eye, about 5 mm in diameter. Dip the looped end into the hydrochloric acid to clean it, and rinse with water. Wipe it dry, taking care not to touch the looped end with your fingers.



2. Clean the graphite carefully with soap or detergent solution, rinse it with water, and dry it.
3. Fill a crucible about half full with lithium chloride,  $\text{LiCl}$ . Put the crucible in a triangle on a ring and ring stand, and heat it gently at first. Later, heat it enough to melt the lithium chloride. **WARNING:** Melted lithium chloride looks like water, but it is hot enough to cause burns, so treat it with care.
4. It is desirable that the melted lithium chloride be as cool as possible, but still molten. It is probably well above its melting point at this stage in your work, so cool it a little by turning down the heat slightly; do not allow it to solidify.
5. With clamps mounted on the ring stand, firmly fix the looped end of the iron wire and one end of the graphite rod in the liquid lithium chloride. Using 2 pieces of copper wire, connect the iron wire to the negative terminal of a 9-volt transistor battery, and connect the graphite electrode to the positive terminal.
6. Observe with care and record your observations. As you watch for several minutes, a drop of liquid lithium metal will form in the loop or iron wire. Withdraw it carefully and let it cool. You will then have a sample of solid metallic lithium. However, if the molten lithium chloride was too hot, the liquid lithium metal will not remain in the iron wire loop. If you have trouble removing the loop and lithium metal, try cooling the molten lithium chloride a bit, before removing the wire loop.
7. Lithium reacts readily with oxygen and with water vapor in the air. If you wish to keep your sample, coat it with melted paraffin, to keep it away from the air. Put the wax-coated sample in a stoppered bottle; do not put it directly in your pocket. (If the wax coating happened to get rubbed off, the lithium in your pocket would react with water vapor and oxygen, forming hydrogen, lithium oxide, and lithium hydroxide. Both lithium oxide and lithium hydroxide are corrosive, destroying cloth and skin. If you wish to handle your lithium sample, use gloves.

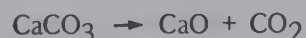
### Questions:

1. Write half-equations which describe the electrolysis of molten lithium chloride.  
*Hint:* Pure molten lithium chloride consists of lithium ions and chloride ions, moving about at random in the liquid state.
2. Suggest equations for the reaction of lithium with oxygen and with water vapor.
3. From your knowledge of electronegativity and considering Group IA of the periodic table, predict how lithium metal will react with water. Will it react more or less vigorously than sodium metal reacts?

## REDOX SECTION 12 • HOW PURE MAGNESIUM AND IRON ARE EXTRACTED

The method used to obtain lithium from lithium chloride is similar to the method used to obtain sodium from salt,  $\text{NaCl}$ , or beryllium, calcium, and boron from their compounds. Magnesium is obtained from the ocean in this way. To

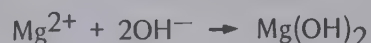
produce magnesium, limestone or oyster shells (both are calcium carbonate,  $\text{CaCO}_3$ ) are first heated to form calcium oxide and carbon dioxide:



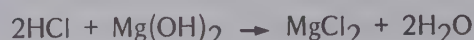
The carbon dioxide passes off as a gas. The solid calcium oxide is mixed with the sea water, forming calcium ions and hydroxide ions in solution:



The hydroxide ions react with the magnesium ions already present naturally in the sea water, to form magnesium hydroxide as an insoluble precipitate:



The magnesium hydroxide solid is filtered off and treated with hydrochloric acid, forming magnesium chloride and water:



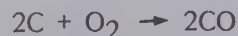
The water is evaporated off. The solid magnesium chloride is melted and then the  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  ions move about at random in the molten substance. The magnesium ions are reduced to metallic magnesium, and the chloride ions are oxidized to gaseous chlorine. The gaseous chlorine, a severe pollutant, is saved and used to make more HCl, for the next batch of magnesium hydroxide.

Magnesium is a useful metal because it is light, low in density, and strong. It is used in aircraft construction, and in the casings of household appliances, such as vacuum cleaners, where light weight is desirable. It is also used to make ladders; these are rather expensive, more costly for example than aluminum ladders, but also lighter, since magnesium has an even lower density than aluminum and is about equally strong.

### Producing Iron—A Different Kind of Oxidation and Reduction

The most common useful metal, iron, is also produced from its ore by an oxidation-reduction reaction. In this case, however, the reaction does not involve electrical oxidation and reduction at electrodes. Instead, the reaction takes place inside a large, chimney-like building called a *blast furnace*.

At the top of the blast furnace, a mixture of iron ore ( $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$ ), limestone ( $\text{CaCO}_3$ ), and coke (a form of carbon, C) is introduced. Inside the blast furnace air is available, and the carbon (coke) is oxidized to carbon monoxide, a gas:



The carbon monoxide reacts with the iron oxide. In this oxidation-reduction reaction, iron is reduced from +3 in iron oxide to zero in metallic iron, while carbon is oxidized from +2 in carbon monoxide to +4 in carbon dioxide:



At the temperatures inside the blast furnace, the iron is a liquid, so as it is formed, it dribbles down to the bottom of the blast furnace and collects as a pool of white hot liquid.

This liquid would oxidize in an instant, back to  $\text{Fe}_2\text{O}_3$ , by combining with the oxygen in the air that is blowing over it, except for one thing. The  $\text{SiO}_2$  that was naturally present in the iron ore reacts with the limestone to form calcium silicate,  $\text{CaSiO}_3$ , and carbon dioxide:



The calcium silicate is a liquid, so it dribbles down too. But it is not soluble in the liquid iron, and it is also less dense than the liquid iron. So it floats on top and prevents the oxygen in the air above the pool of iron from reacting with the molten iron.

The molten iron that is produced in a blast furnace is not pure. It contains carbon as a major impurity, and often dissolved phosphorus, sulfur, and various other metals from the impurities that were present in the iron ore, or in the coke or the limestone. When this molten iron with its dissolved substances is poured into molds and cooled, it solidifies. The solid iron is called *cast iron*, or *pig iron*. The impure iron can be purified by additional processing in open hearth furnaces, or so-called electric furnaces, or even in the old-fashioned Bessemer converters, to make the much more useful varieties of steel—iron plus a controlled amount of carbon and sometimes other elements—that people use every day.

## REDOX EXPERIMENT 15 • A CURE FOR BALDNESS?

Now that you have read the details about how magnesium and iron are extracted, it is probably about time for something useless but interesting. Here is a way to grow hair on aluminum foil (and as you can see from one of the illustrations in your text, one of the authors would like to make this into a practical development!).

### Purpose:

To observe the controlled burning of a metal in an oxidation-reduction reaction.

### Materials:

0.3 g  $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$   
10 cc water  
13-mm x 100-mm test tube  
piece of aluminum foil, about 5 cm by 5 mm  
emery cloth

### Procedure:

1. In the test tube dissolve the mercury(II) nitrate in 10 cc of water.



2. Clean one end of the strip of aluminum foil by rubbing it briskly with emery cloth, to scour off the coating of aluminum oxide.
3. Immediately dip the scoured end as quickly as possible into and out of the mercury(II) nitrate solution. Continue to hold the foil in your hand by the other end, and watch the scoured end closely. Make a record of all you observe, and of anything unexpected that you yourself do.

### Question to Ponder:

Why, do you suppose, was it necessary to first dip the aluminum foil into the mercury(II) nitrate solution before anything observable happened?

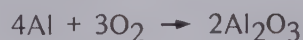
## REDOX SECTION 13 • HOW ALUMINUM GETS HAIRY

In the last experiment two different oxidation-reduction reactions took place. First, when the aluminum was dipped into the mercury(II) nitrate solution, this happened:



Mercury ions were reduced to metallic mercury while metallic aluminum was oxidized to aluminum ions. The metallic mercury that was formed deposited on the surface of the aluminum metal, and then dissolved in it. This is an example of a liquid, mercury, dissolving in a solid, aluminum.

When you then exposed the piece of foil to the air, this happened:



This reaction is exothermic; you may have noticed that the foil became warm, perhaps so hot that you let go of it. In this reaction, as you can see, aluminum is oxidized and oxygen is reduced. Ordinarily, the aluminum oxide that is formed will adhere tightly to the surface of the aluminum foil, and prevent any more oxygen from reacting with the aluminum underneath the aluminum oxide coating. But in this case, mercury is dissolved in the aluminum, and aluminum oxide cannot adhere tightly to that solution of mercury and aluminum. So, the aluminum continues to be oxidized by the oxygen in the air, forming filaments, or hair-like structures, of aluminum oxide that grow longer before your eyes.

Next we can try another exothermic oxidation-reduction reaction.

## REDOX EXPERIMENT 16 • THE COMBUSTION OF AMMONIA IN AIR

Ammonia will react with oxygen in the air to form water vapor and nitrogen. This reaction takes place rapidly when ammonia gas is heated slightly in the presence of copper metal and air.

### Purpose:

To observe an interesting oxidation-reduction reaction.

### Materials:

uninsulated copper wire, about 30 cm long  
pencil or glass stirring rod  
1M HCl  
10 cc concentrated ammonia water  
250-cc Erlenmeyer flask

### Procedure:

1. Wind the copper wire 7 or 8 times around the pencil or stirring rod to make a helix (which some people incorrectly call a spiral). Leave about 5 or 6 cm of the wire unwound for a straight handle. Remove the pencil or stirring rod. Bend the handle at right angles to the helix.
2. Dip the helix into the hydrochloric acid to clean it, then remove and rinse it with water.
3. Put the concentrated ammonia water into the Erlenmeyer flask. Heat the tip of the copper helix in a gas flame until it is red hot, then immediately insert it part way into the Erlenmeyer flask, so that it remains completely out of the ammonia water in the bottom of the flask.
4. Record your observations. (If nothing happens when you insert the copper helix in the flask, repeat the procedure, transferring the helix from the flame to the flask as quickly as possible so that the wire is still hot by the time it gets inside the flask.)

### Questions:

1. Write a balanced equation for the reaction that you have observed.
2. Identify the elements or compounds which are oxidized and which are reduced.

## REDOX SECTION 14 • PHOTOGRAPHY AND OXIDATION-REDUCTION REACTIONS

In your work with the aluminum foil and with the ammonia water, the oxidation-reduction reaction was visible; it took place right before your eyes. Both reactions were interesting, but not very practical. As you have perhaps guessed, though, there *are* practical examples of these kinds of oxidation-reduction reactions. One of them is in photography. Ordinary black-and-white photographic film is mostly a layer of gelatin on a flexible transparent piece of plastic. This is purchased rolled up, either with paper around it or inside a metal cartridge to keep the light out.

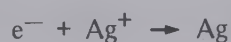
In that gelatin layer there are tiny particles of solid silver bromide. In an ordinary roll of film there are about 10 billion particles of silver bromide distributed in the layer of gelatin, and their total weight is about 0.001 gram. So you can see that the particles of silver bromide are very, very small.

### Absorption of Light Energy

When the film is exposed to light for a fraction of a second, when the picture

is taken, the light energy is absorbed by whichever silver bromide particles happen to be in the places where the light hits the gelatin layer. For example, if you were taking a picture of a Karate expert who was wearing a white gown and a black belt, light reflected off the gown into the camera would affect some of the silver bromide particles. But since no light (or very little) would be reflected off the black belt, the silver bromide particles that correspond to the image of the belt on the gelatin layer would not have absorbed any light energy.

Later on, when the film is developed, an oxidation-reduction reaction takes place rapidly at the silver bromide particles that absorbed light energy. The silver bromide particles that did not absorb light energy do not react rapidly at all. The developer solution (there are many substances which can be used) supplies electrons that cause the following reduction half-reaction:



Since the developer furnishes the necessary electrons, it is therefore oxidized itself. So, as the film is developed, tiny particles of silver metal appear wherever light originally hit the film in the camera. Very finely divided silver particles appear black, not shiny like ordinary silver. The developed film now carries a reversed image; it is a *negative*. You would see a black-robed karate expert wearing a white belt.

Next, the unreduced silver bromide particles are dissolved out of the gelatin layer. This is called *fixing*, and the solution that dissolved the particles is called *hypo* or *fixer*. If the particles were not dissolved out, they would be affected by the light when we looked at the negative and eventually the whole picture would turn black.

### A Positive Picture

To make a picture with a positive image--our karate player with a white robe and a black belt--it is necessary to go through the whole process once more, this time using a layer of gelatin with silver bromide particles on a white paper base. This process is called *printing*. For this, we can place the negative between a source of light and a piece of printing paper (the gelatin layer and silver bromide particles on a paper base). Then the printing paper is exposed to light that passes through the negative. This time, wherever the negative is black, no light gets through; wherever the negative is transparent, light does get through and is absorbed by the silver bromide particles in the printing paper. So, when it is developed, wherever the negative was transparent, the picture is black; wherever the negative was black, the picture is white. The print paper then carries a positive image.

Just as with the negative, the printing paper has to be fixed after it is developed, to dissolve away the unreduced silver bromide particles. Otherwise, the picture would turn dark all over.

## REDOX EXPERIMENT 17 • REMOVING TARNISH FROM SILVER

This has been a long discussion; no doubt the time is ripe to conclude our excursion into one of the most interesting parts of chemistry. So to wrap it



up with a really practical application, we will learn how to remove tarnish from silver chemically, with no hard, tiresome, polishing effort.

**Purpose:**

To learn the details of a practical application of oxidation-reduction reactions: the removal of tarnish from silver.

**Materials:**

one or more pieces of tarnished silverware  
piece of aluminum foil large enough to wrap the silverware in  
50 g baking soda ( $\text{NaHCO}_3$ ) or salt ( $\text{NaCl}$ )  
large beaker or pan, big enough to hold the wrapped silverware

**Procedure:**

1. Fill the large container about half full with water, and pour in the baking soda or salt. (All we really need is a water solution of ions, so any non-poisonous ionic compound will do.) Stir until the baking soda is dissolved.
2. Put the piece of aluminum foil under the water, on the bottom of the container. Be sure there are no bubbles caught under the foil. Lay the tarnished silverware on top of the foil and wrap the foil around the silverware, taking care not to leave any bubbles within the wrapping.
3. Heat the water in the container until it is almost boiling. (It does no harm if the water boils a little.) Keep the water almost at the boiling point for about 15 minutes; if the silver is extremely tarnished, keep the water boiling longer. Let the water cool, and unwrap the bright and shining silverware.

**Questions:**

Black silver tarnish is silver sulfide,  $\text{Ag}_2\text{S}$ . In this reaction, the silver ions in the tarnish are reduced to metallic silver, while the aluminum is oxidized to  $\text{Al}^{3+}$  ions. Write a pair of half-equations for the oxidation and reduction half-reactions.

**SUGGESTIONS FOR CREATIVE WORK**

Following is a summary of suggestions for creative work that have been mentioned throughout this module. If you have not had a chance to try any of these yet, we hope you will spend some time now doing creative work.

1. Make your own storage battery.
2. Test your predictions about the effectiveness of metals that may be used to prevent the corrosion of iron.
3. Repeat Redox Experiment 7 (Taking Water Apart), using potassium iodide as the solute in place of ammonium chloride.

4. Try some of the optional experiments (the Nickel Egg, Duplicating Medals and Buttons, The Golden Touch).
5. Prepare some etchings by the electrical method described in Redox Experiment 13, Electroetching.

## SUGGESTIONS FOR CREATIVE WRITING

1. Write an article for teen-age automobile owners explaining the principle of the storage battery. Include such items as why it is necessary to add more water at intervals and why more acid need not be added, and explain which is in greater danger of freezing in winter: a fully charged battery or one that is nearly run down.
2. Write an article for a photo magazine in which you explain the chemical reactions involved in developing, fixing, and printing pictures taken on black and white film.
3. Write an article for home owners in which you alert them to areas especially susceptible to corrosion and suggest ways they can prevent this.
4. Investigate the oxidation-reduction reactions that occur to cause "spontaneous combustion." Apply these principles in an article designed to alert people to areas of potential danger in their homes. *Hint:* Why is it dangerous to toss oily dustcloths and dustmops in a closet?

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Why the best way to keep the chromium plated trim on your car from rusting is either to take it off, or store the car in a garage built in in a very dry desert.

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Dillard, C. R., and Kammeyer, P. H., *J. Chem. Ed.*, 40, 363 (1963).

How to make and use a whole set of different half-cells, combining them in different ways as whole cells. Highly recommended.

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A full discussion on the photographic process, including oxidation and reduction, plus a lot more. Instead of white-gowned, black-belted karate experts, this article uses white-black penguins.

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A historical and chemical discussion on magnesium, with more details about its extraction from the sea.

Ritz, W. C., "Photographing the Lead Tree Reaction," *Chemistry*, September 1970, p. 28.

On "lead trees," closely related to Redox Experiment 3. Very enjoyable, and beautiful to see.

Szabadvary, Ferenc, "Early Electrical History," *Chemistry*, December 1972, p. 11.

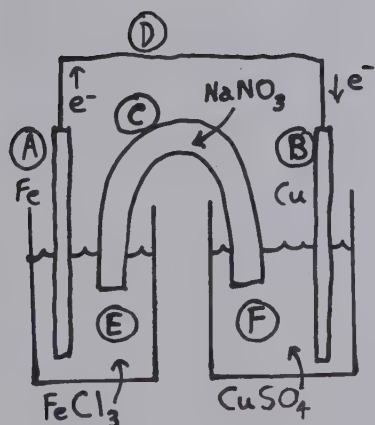
All about Luigi Galvani and how he happened to make the first cell. Also contains details about Volta's work, and how he made successful batteries called Voltaic piles.

Weissman, Eugene Y., "Batteries, the Workhorses of Chemical Energy Conversion," *Chemistry*, November 1972.

An excellent and thorough discussion of all sorts of cells and batteries with the complete chemical equations that apply. Highly recommended.

## PRACTICE EXERCISES (Answers on pp. 60, 61)

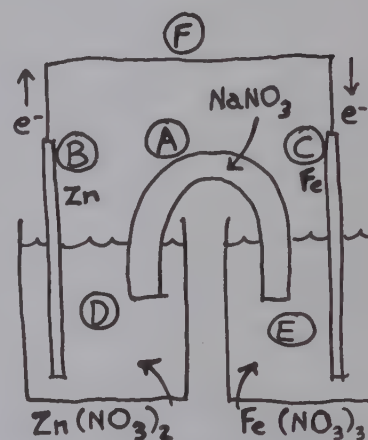
- For each of the following metals and ions, write an oxidation half-equation for the metal and a reduction half-equation for its ion.
  - Mg,  $\text{Mg}^{2+}$
  - Cu,  $\text{Cu}^{2+}$
  - Zn,  $\text{Zn}^{2+}$
  - Pb,  $\text{Pb}^{2+}$
  - Fe,  $\text{Fe}^{2+}$
  - Fe,  $\text{Fe}^{3+}$
  - Al,  $\text{Al}^{3+}$
  - Ag,  $\text{Ag}^+$
- Using the half-equations you write for Question 1, write balanced complete equations for the following oxidation-reduction reactions.
  - $\text{Mg} + \text{Cu}^{2+}$
  - $\text{Zn} + \text{Pb}^{2+}$
  - $\text{Zn} + \text{Fe}^{3+}$
  - $\text{Al} + \text{Ag}^+$
- Give the oxidation number for each element in the following formulas.
  - Cd
  - $\text{O}_2$
  - $\text{Al}^{3+}$
  - $\text{MnO}_2$
  - $\text{Ca}(\text{ClO}_3)_2$
  - $\text{K}_2\text{Cr}_2\text{O}_7$
- Write the half-equation for the reduction of water. (*Hint:* The products of the reaction are gaseous hydrogen and hydroxide ions.)
  - Write the half-equation for the oxidation of water. (*Hint:* The products of the reaction are hydronium ions and gaseous oxygen.)
- Using the half-equations you wrote for Questions 1 and 4, write balanced complete equations for the following oxidation-reduction reactions.
  - $\text{Mg} + \text{H}_2\text{O}$
  - $\text{Fe} + \text{H}_2\text{O}$
- For each complete equation you wrote for Question 5, list the oxidation number of each element in each term of the equation, and state what was oxidized and what was reduced in the reaction.
- Combine the half-equations you wrote for the oxidation and reduction of water (Question 4) to obtain a balanced complete equation for the electrolysis of water. Write this equation in simplest form. List the oxidation number of each element in each term of the equation, and state what was oxidized and what was reduced in the reaction.
- Explain how you would determine experimentally whether lead or zinc is more easily oxidized. Describe what materials and apparatus you would use, how you would use them, and for what experimental evidence you would look.
- In the copper-magnesium cell, explain why the magnesium ribbon lost weight while the copper strip gained weight.
- Apply the principles of oxidation-reduction to explain why iron rusts. What implications does this have for preventing corrosion?
- Apply the principles of oxidation-reduction to explain how jewelry is plated with silver.
- Describe a method for "counting" electrons.
- Show how oxidation-reduction is important in *one* of the following processes: production of photographic images, extracting iron from its ore, operation of a storage battery, removing tarnish from silver.
- Refer to the accompanying diagram and match the letters with the appropriate terms: electrodes, metal being oxidized, ions being reduced, region of electron flow, region in which ions are present.





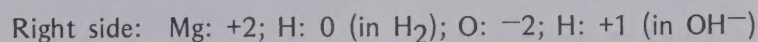
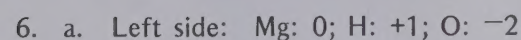
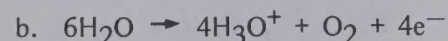
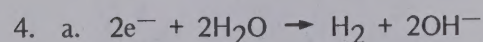
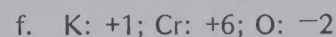
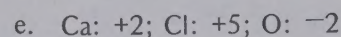
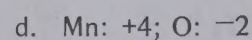
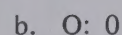
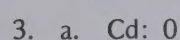
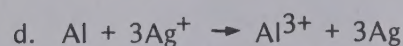
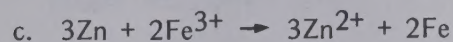
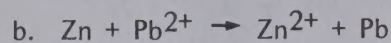
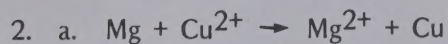
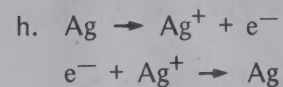
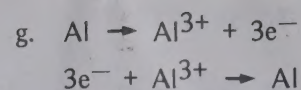
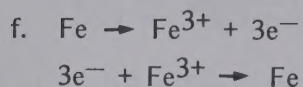
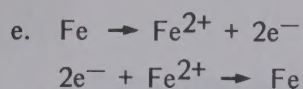
## SELF-TEST (Answers on p. 62)

- For each of the following metals and ions, write an oxidation half-equation for the metal and a reduction half-equation for its ion.
  - Zn,  $\text{Zn}^{2+}$
  - Fe,  $\text{Fe}^{3+}$
  - Ag,  $\text{Ag}^+$
  - Cd,  $\text{Cd}^{2+}$
  - Cu,  $\text{Cu}^{2+}$
  - Mg,  $\text{Mg}^{2+}$
- Using the half-equations you wrote for Question 1, write balanced complete equations for the following oxidation-reduction reactions.
  - $\text{Zn} + \text{Cu}^{2+}$
  - $\text{Fe} + \text{Cu}^{2+}$
  - $\text{Zn} + \text{Fe}^{3+}$
  - $\text{Mg} + \text{Cu}^{2+}$
- Give the oxidation number for each element in the following formulas.
  - Fe
  - $\text{H}_2$
  - $\text{CuCl}_2$
  - $\text{OH}^-$
  - $\text{H}_2\text{SO}_4$
  - CO
- For each of the following oxidation-reduction reactions write half-equations and then combine them into a balanced complete equation for the reaction.
  - $\text{Al} + \text{Ag}^+$  (products:  $\text{Al}^{3+}$ , Ag)
  - $\text{Mg} + \text{H}_2\text{O}$  (products:  $\text{Mg}^{2+}$ ,  $\text{H}_2$ ,  $\text{OH}^-$ )
- For each of the following complete equations, determine what was oxidized and what was reduced.
  - $\text{Zn} + 2\text{MnO}_2 \rightarrow \text{ZnMn}_2\text{O}_4$
  - $\text{Pb} + \text{PbO}_2 + 2\text{SO}_4^{2-} + 4\text{H}_3\text{O}^+ \rightarrow 2\text{PbSO}_4 + 6\text{H}_2\text{O}$
- Explain why a piece of iron will lose weight and a piece of copper will gain weight when the iron is placed in an  $\text{FeCl}_3$  solution, the copper is placed in a  $\text{CuSO}_4$  solution, a salt bridge is placed into the two solutions, and the metals are connected with a copper wire.
- Explain how you would determine experimentally whether aluminum or zinc is more easily oxidized. Describe what materials and apparatus you would use, how you would use them, and for what experimental evidence you would look.
- Refer to the accompanying diagram and match the letters with the appropriate term: electrodes, ions being reduced, metal being oxidized, regions of electron flow, regions in which ions are present.
- Describe a method for "counting" electrons.
- Select one area in your daily living or in an industrial or commercial process in which oxidation-reduction occurs. Apply the principles you have learned in this module to show how oxidation-reduction is used in the process.



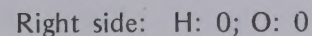
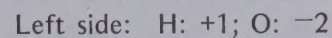
## ANSWERS TO PRACTICE EXERCISES

- $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$  (oxidation)  
 $2\text{e}^- + \text{Mg}^{2+} \rightarrow \text{Mg}$  (reduction)
  - $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$   
 $2\text{e}^- + \text{Cu}^{2+} \rightarrow \text{Cu}$
  - $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$   
 $2\text{e}^- + \text{Zn}^{2+} \rightarrow \text{Zn}$
  - $\text{Pb} \rightarrow \text{Pb}^{2+} + 2\text{e}^-$   
 $2\text{e}^- + \text{Pb}^{2+} \rightarrow \text{Pb}$



The Mg was oxidized from 0 to +2, while some of the H was reduced from +1 to 0.

b. Same answer as a, if Fe is substituted wherever Mg appears in answer.



Oxygen was oxidized from -2 to 0, while hydrogen was reduced from +1 to 0.

8. Follow procedure of Redox Exp. 2, using pieces of lead and zinc and solutions of a lead salt and a zinc salt.

9. Mg atoms went into solution as  $\text{Mg}^{2+}$  ions.  $\text{Cu}^{2+}$  ions deposited on the Cu strip as Cu atoms.

10. See Redox Sec. 8.

11. See Redox Sec. 10.

12. See Redox Sec. 10.

13. For photographic images, see Redox Sec. 14; for iron extraction, see Redox Sec. 12; for the storage battery, see Redox Sec. 7; and for tarnish removal, see Redox Exp. 17.

14. Electrodes: A, B; metal being oxidized: A; ions being reduced: F; region of electron flow: A, D, B; regions in which ions are present: C, E, F.



# ANSWERS TO SELF-TEST

## ANSWERS TO SELF-TEST

1. a.  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$  (oxidation)  
 $2\text{e}^- + \text{Zn}^{2+} \rightarrow \text{Zn}$  (reduction)
- b.  $\text{Fe} \rightarrow \text{Fe}^{3+} + 3\text{e}^-$   
 $3\text{e}^- + \text{Fe}^{3+} \rightarrow \text{Fe}$
- c.  $\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$   
 $\text{e}^- + \text{Ag}^+ \rightarrow \text{Ag}$
- d.  $\text{Cd} \rightarrow \text{Cd}^{2+} + 2\text{e}^-$   
 $2\text{e}^- + \text{Cd}^{2+} \rightarrow \text{Cd}$
- e.  $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$   
 $2\text{e}^- + \text{Cu}^{2+} \rightarrow \text{Cu}$
- f.  $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$   
 $2\text{e}^- + \text{Mg}^{2+} \rightarrow \text{Mg}$

2. a.  $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$
- b.  $2\text{Fe} + 3\text{Cu}^{2+} \rightarrow 2\text{Fe}^{3+} + 3\text{Cu}$
- c.  $3\text{Zn} + 2\text{Fe}^{3+} \rightarrow 3\text{Zn}^{2+} + 2\text{Fe}$
- d.  $\text{Mg} + \text{Cu}^{2+} \rightarrow \text{Mg}^{2+} + \text{Cu}$

3. a. Fe: 0
- b. H: 0
- c. Cu: +1; Cl: -1
- d. O: -2; H: +1
- e. H: +1; S: +6; O: -2
- f. C: +2; O: -2

4. a.  $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$   
 $\text{e}^- + \text{Ag}^+ \rightarrow \text{Ag}$  (multiply equation by 3)  
 $\text{Al} + 3\text{Ag}^+ \rightarrow \text{Al}^{3+} + 3\text{Ag}$
- b.  $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$   
 $2\text{e}^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{OH}^-$   
 $\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + \text{H}_2 + 2\text{OH}^-$

5. a. Oxidation number of zinc changed from 0 to +2, so zinc was oxidized.  
Ox. no. of manganese changed from +4 to +3, so manganese was reduced.  
Ox. no. of oxygen did not change; it was neither oxidized nor reduced.
- b. Ox. no. of free lead atoms changed from 0 to +2, so free lead atoms were oxidized. Ox. no. of lead in  $\text{PbO}_2$  changed from +4 to +2, so lead in  $\text{PbO}_2$  was reduced. Sulfur, oxygen, and hydrogen had no change in ox. no., so they were neither reduced nor oxidized.
6. Fe atoms go into the solution as  $\text{Fe}^{3+}$  ions.  $\text{Cu}^{2+}$  ions deposit on the Cu strip as Cu atoms.
7. Follow procedure of Redox Exp. 2, using pieces of aluminum and zinc and solutions of an aluminum salt and a zinc salt.
8. Electrodes: B, C; ions being reduced: E; metal being oxidized: B; region of electron flow: B, F, C; regions in which ions are present: A, D, E.
9. See Redox Sec. 10.
10. Answer depends on selection.

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KEYS TO CHEMISTRY

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## EQUIPMENT AND SUPPLIES LIST

The following equipment and supplies should be available to each student who works through this module. Many of these materials are not consumed in the experiments and therefore will suffice for an entire class in the amounts indicated.

### Glassware or Plasticware

- 1 Beaker, 50 cc
- 4 Beakers, 250 cc
- 1 Beaker, 1000 cc
- 1 Flask, Erlenmeyer, 250 cc
- 1 Rod, stirring
- 1 Test tube, 13 mm x 100 mm
- 16 Test tubes, 18 mm x 150 mm
- 1 Thermometer, range  $-10^{\circ}\text{C}$  to  $110^{\circ}\text{C}$
- 1 Watch glass, 75-mm diameter

### Hardware

- 1 Burner
- 2 Clamps, buret
- 1 Crucible, porcelain, size 0
- 1 Ring, iron
- 1 Test tube rack
- 1 Triangle
- 1 Voltmeter or VOM, range 0 to 3 volts or 0 to 10 volts

### Chemical Supplies

- 8 g Acid, boric (optional)
- 100 cc Acid, hydrochloric, 1M solution
- 10 cc Acid, nitric, 3M solution
- 3.0 g Agar
- 12 cc Ammonia water, conc.
- 1 g Ammonium chloride
- 15 cm Chromel wire (optional)
- 7 Copper foil strips, about 5 mm x 15 cm
- 2 m Copper wire, bare
- 2 m Copper wire, insulated
- 50 cc Copper(II) chloride, 1M solution
- 150 cc Copper(II) sulfate, 1M solution
- 1 g Graphite, powdered (optional)
- 100 cc Iron(III) chloride, 1M solution
- 5 Lead strips, about 2 mm x 30 mm
- 100 cc Lead(II) acetate, 1M solution
- 15 g Lithium chloride
- 30 cm Magnesium ribbon
- 25 cc Magnesium nitrate (or chloride), 1M solution
- 15 g Nickel chloride, hydrated (optional)
- 55 g Nickel sulfate, hydrated
- 1 pc Paper, filter
- 6 cc Phenolphthalein, 0.05% solution in 1:1 alcohol and water
- 0.5 g Potassium cyanide (optional)
- 12 cc Potassium ferricyanide,  $\text{K}_3\text{Fe}(\text{CN})_6$ , 1% water solution
- 50 cc Silver nitrate, 0.5M solution
- 50 g Sodium chloride
- 50 g Sodium hydrogen carbonate
- 10 cc Sodium hydroxide, 3M solution
- 50 cc Sodium sulfate, 1M solution
- 2 pc Test paper, litmus or Hydrion pH
- 6 Zinc strips, about 2 mm x 30 mm
- 100 cc Zinc nitrate, 1M solution

### Locally Obtainable Supplies

- 1 bx Aluminum foil (class supply)
- 1 Bag of porous cloth
- 1 Battery, 9-volt transistor
- 1 Bottle, stoppered (optional)
- 1 Bulb, flashlight, 1.5-volt
- 1 Bulb, flash
- 4 Clips, alligator
- 1 pc Cotton cloth, tightly woven, about 20 cm x 20 cm
- 6 cc Detergent
- 1 Egg, hen's (optional)
- 2 Electrodes, carbon or graphite, can be pencil "leads" or center electrodes of discarded Leclanche cells
- 1 Emery cloth, about 5 cm x 5 cm
- 1 Flower pot with moist soil
- 1 pr Gloves, rubber
- 6 cm<sup>2</sup> Gold foil (optional)
- 1 Iron wire (coat hanger)
- 1 Jewelry or coin to be gold-plated (optional)


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**RECOMMENDED FOR USE  
IN ALBERTA SCHOOLS**



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